**Experiment 12: Qualitative Analysis of Cations**

*Pre-Laboratory Assignment*

The pre-lab assignment for Part A of the experiment is to complete the flow chart

and answer the question on page 10 of this document. There is **no** pre-lab

assignment for Part B.

**Objective:** To separate different cations in aqueous mixtures using selective

precipitation and to confirm their identities using chemical tests.

**Introduction**

The Eagle Art Studio and Print Shop had finally found an appropriate space to

rent near the center of town. They were able to move into a large vacant room

overlooking the baseball diamond and playground of Milford Park. However, the

location of an art studio near the park had some of the town residents worried. What if

the paints, inks and ceramic pigments that the artists used were being poured into the

sinks? Could the metallic components responsible for the colors get into the

groundwater?

The Town Council contacted the Massachusetts Water Resource Authority, which

scheduled tests to be run on the water coming out of the studio. The owners of the shop

decided they should do some of their own tests on samples from the sink traps in the

building in order to determine what metallic cations their employees might be discarding

into the drains.

**Principles of the Qualitative Analysis of Cations**

The process of finding out *what* compounds are contained in a sample is called

***qualitative analysis***. The process of finding out *how much* of a compound is contained in

a sample is called ***quantitative analysis***. You have used several *quantitative* analysis

techniques, such as titration and spectrophotometry. During the next three weeks, you

will use *qualitative* analysis techniques in order to determine what metallic cations are

contained in aqueous solutions that are provided for you. These techniques will allow

you to both separate the cations in the mixture as well as to identify them.

The various salts of the cations that you will be studying have varying solubilities

in water. The differences in solubilities of these salts can be exploited in such a way as to

allow for separation of the cations. As an example, let’s examine the cations calcium,

Ca2+, and sodium, Na+. Calcium chloride is readily soluble in water, while calcium

hydroxide is highly insoluble in water. By contrast, sodium chloride and sodium

hydroxide are both readily soluble in water. An aqueous solution which contains a

mixture of calcium chloride and sodium chloride can be treated with an aqueous solution

that contains hydroxide ions. The result of such treatment will be the formation of a solid

precipitate that is composed of insoluble calcium hydroxide. The sodium hydroxide, on

the other hand, remains dissolved in the water. The solid material that contains the

calcium ions can be separated from the aqueous solution containing the sodium ions

using a technique such as filtration.

In summary, the addition of an appropriate chemical reagent to an aqueous

mixture of cations can selectively cause one or more of the cations to form a solid

precipitate while one or more of the cations will remain dissolved in the water, thus

2

allowing for separation. (Pages 749-754 in Tro also discuss principles involved in

qualitative analysis.)

**General Procedures for the Qualitative Analysis of Cations**

*Avoiding Contamination*

As you follow the procedures for separating and identifying the cations in a

mixture, it will be extremely important to avoid contamination of the samples and

chemical reagents at all times. The presence of a contaminant that contains a cation will

lead to a false positive result; therefore, it is critical that all glassware be thoroughly

cleaned before it is used and should remain clean throughout the procedure. Laying a

glass stirring rod on a dirty lab bench, for instance, could lead to contamination.

Touching the tip of a medicine dropper to the side of a test tube could cause contaminants

to be picked up and transferred to another solution. In addition, all water used for these

procedures must come from the plastic, white faucets in the lab that deliver de-ionized

water. Tap water from the regular faucets contains a wide variety of ions and could result

in misleading observations.

*Equipment and Chemicals*

The tests that you will perform to identify the cations after they have been

separated require only very small amounts of sample. Therefore, you will work with the

smallest size test tubes available (10 x 75 mm), thin glass stirring rods and medicine

droppers. Rather than measuring volumes of liquids with a graduated cylinder, it will be

easier to simply count the number of drops of liquid dispensed from a medicine dropper.

In general, it is safe to assume that *20 drops from a medicine dropper is equivalent to*

*1 mL of solution*. You will usually be told exactly how many drops to add in any given

step of the procedure. As mentioned previously, it is very important that the medicine

droppers **never** become contaminated, for instance, by allowing the tip to touch either the

surface of a solution or the side of a test tube.

The chemical reagents for the qualitative analysis procedures are aqueous

solutions that are contained in dropper bottles. The caps of these bottles are labeled. Do

not put the wrong dropper into a bottle, or the entire contents of the bottle will become

contaminated! When you have finished using the bottle, screw the cap back on *tightly*. If

the cap is not on tight, the next person to grab it by the dropper will knock the bottle over.

In addition, some of the water will evaporate if the cap is not on tight, and this will alter

the concentration of the solution.

*Mixing*

After a reagent has been added to a solution in a test tube, it is very important that

the solutions are stirred together thoroughly. Reactions cannot proceed to completion

unless the reactants come into intimate contact with each other. Use a *thin* stirring rod to

mix the liquids so that the contents of the test tube do not overflow. Of course, the

stirring rod must be rinsed well with de-ionized water before being used.

*Checking Acidity/Basicity*

In many cases during the separation of cations, an acid or base solution is added

to a sample until the pH of the solution becomes either acidic or basic. In these instances,

litmus paper is used to monitor the pH. A drop of the solution being tested is removed

from the test tube using a glass stirring rod. The rod is touched to the litmus paper, and

3

the color of the paper indicates whether the pH is basic (blue) or acidic (red). The litmus

paper must never be placed directly into the solution! It is possible to use litmus paper to

observe if a solution is weakly acidic or basic as opposed to strongly acidic or basic. A

strong acid or base will turn litmus paper a more intense color than will a weak acid or

base.

*Forming, Separating and Washing Precipitates*

When an appropriate chemical reagent is added to a solution containing a mixture

of cations, a precipitate will form that is composed of the insoluble salt(s) of one or more

of the cations. This solid precipitate can be separated from the aqueous solution, which

contains the soluble salt(s) of the remaining cations, by filtration; however, a more

convenient technique for the separation of a solid from a liquid is centrifugation. A test

tube containing the mixture is placed in a centrifuge, which spins the mixture at a very

high speed. The resulting centrifugal force packs the solid material tightly into the

bottom of the test tube. The liquid supernatant can then be easily poured away, or

*decanted*, from the solid. Read about Using a Centrifuge in TECH Section VI.

Before the liquid supernatant is decanted from the solid material, it is a good idea

to check for complete precipitation. After centrifuging the mixture, add one or two more

drops of the reagent which caused precipitation to occur. Watch the supernatant carefully

to see if more precipitate forms. If no more precipitate forms, then precipitation is

complete and the supernatant may be poured off. If more solid does appear in the

supernatant, add another drop or two of the reagent solution, thoroughly stir the contents

of the test tube, and place it back in the centrifuge for two minutes. The process of

checking for complete precipitation should continue until no solid appears in the

supernatant upon addition of the reagent.

After the liquid has been decanted from the solid, a small amount of this solution

will remain behind in the test tube with the solid. In order to completely remove this

liquid and any contaminants that it contains, the precipitate is washed with water. Ten to

fifteen drops of water are added to the test tube, and the mixture of solid and liquid is

thoroughly stirred with a glass rod. The test tube is place in a centrifuge for two minutes,

then the water is decanted away from the solid and may be disposed of down the drain.

Solids are usually washed two times before proceeding to the next step in the procedure.

*Heating Solutions*

Occasionally, a step in a qualitative analysis procedure will require that a solution

or mixture be heated. A water bath usually provides a high enough temperature. Place

about 150 mL of water in a 250 mL beaker and heat it on a hot plate. A metal *beaker*

*cover* with four holes in it is available in your drawer. This metal plate can be placed on

top of the beaker, and 10 x 75 mm test tubes can be inserted into the holes such that the

bottom of the test tube is positioned in the middle of the boiling water. It can take some

time for the water to reach the boiling point, so if you know you will require a water bath

at some point in the procedure, you should set the water on a hot plate at the beginning of

the lab period.

*Labeling*

During the qualitative analysis procedures, you will be manipulating a large

number of test tubes with a variety of contents. It is vital that everything be clearly and

properly labeled. Solutions and solids can be inadvertently discarded if test tubes do not

4

have accurate labels. Also, before you place one of your test tubes in the centrifuge with

other students’ test tubes, you must label it with your name.

*Laboratory Notebook*

As always, you must record very complete and descriptive observations in your

lab notebook throughout the qualitative analysis procedures. You might find it useful to

organize your observations in a table. Color changes, the presence or absence of

cloudiness and the formation of bubbles are all relevant observations that must be

carefully noted. You should record the color of solutions *before* they are added to each

other, as well as what happens after they are mixed together. Remember that there is a

difference between the terms *clear* and *colorless*. To say that a liquid is “clear” indicates

that no solid material is present, while the absence of color is best described by the word

“colorless”. For instance, if two non-colored solutions are mixed together and a white

precipitate forms, the correct observation is a “colorless and cloudy” mixture.

Your TA will collect the carbon copies of your notebook pages at the end of each

of the qualitative analysis lab periods. Because you will be performing the qualitative

analyses over three lab periods, it is especially important that you record completely what

you did and what you observed in lab each day. You will need to refer to observations

from the previous lab periods in order to successfully complete the analyses.

*Hazardous Chemical Byproducts*

Some of the chemical reagents and cations that you will work with during the

qualitative analysis procedures are toxic. These materials present a hazard to the

environment and must be collected in the **Laboratory Byproducts** jars. Those

chemicals that are not hazardous may be safely poured down the drain. Read carefully

the instructions provided for each experiment, and listen to your instructor’s pre-lab talk

to learn which materials may be disposed of in the sink and which must be collected in a

Byproducts jar. Ask your TA if you have any questions regarding the proper disposal of

a chemical.

*Safety Precautions*

The standard safety rules must be followed when carrying out the qualitative

analysis procedures. You must wear both a lab apron and chemical splash goggles.

Some of the reactions that occur will generate hazardous fumes such as ammonia, so it is

prudent to work in the fume hood whenever possible. Read the labels of reagent bottles

carefully to be sure you have chosen the right chemical and the right concentration.

**The Analyses**

In the first week of the qualitative analysis sequence, you will be given explicit

instructions to follow in order to separate the cations Ag+, Fe3+ and Co2+ and confirm

their presence (Part A). In the second and third weeks, you will have to devise your own

scheme for separating the cations ZrO2+, Ni2+, Pb2+ and Al3+ (Part B). In both Parts A

and B, you will first be provided with a solution that contains all of the cations in

question. After you have successfully followed the procedure to separate and confirm

their presence, you will be given an “unknown” solution that contains one or more of the

indicated cations. By following the same procedure that you used for the “known”

solution, you will be able to identify which of the cations are present in the “unknown”

solution.

5

**Part A. Analyzing Solutions for Silver (I), Iron (III) and Cobalt (II) Ions**

The first step in the separation of these three cations involves the precipitation of

the silver ion as the insoluble silver chloride salt. This precipitation is accomplished

simply through the addition of hydrochloric acid.

Ag+ (*aq*) + HCl (*aq*) AgCl (*s*) + H+ (*aq*) **Eq. 1**

Since neither iron (III) nor cobalt (II) forms an insoluble chloride salt, the silver can then

be separated from the other two cations by centrifuging the test tube and decanting the

supernatant. A test is next performed to confirm the presence of silver in the precipitate

that remains in the test tube. First, ammonia is added, which results in dissolution of the

silver (I) compound.

AgCl (*s*) + 2 NH3 (*aq*) Ag(NH3)2

+ (*aq*) + Cl– (*aq*) **Eq. 2**

Adding nitric acid will shift the equilibrium to the left as the acid reacts with the

ammonia, NH3, causing the silver ion to re-precipitate as silver chloride.

The supernatant that was decanted earlier contains both Fe3+ and Co2+. Addition

of ammonia to this solution causes the iron (III) ion to form an insoluble hydroxide and

precipitate out of solution.

Fe3+ (*aq*) + 3 NH3 (*aq*) + 3 H2O (*l*) Fe(OH)3 (*s*) + 3 NH4

+ (*aq*) **Eq. 3**

Centrifugation and decantation leaves Fe(OH)3 solid which can be dissolved in hot

hydrochloric acid. There are two confirmation tests for iron (III), and you will perform

both. In the first, addition of potassium thiocyanate solution produces a red-brown color

if Fe3+ is present.

Fe3+ (*aq*) + SCN– (*aq*) Fe(SCN)2+ (*aq*, red-brown) **Eq. 4**

In the second test, ammonia is first added until the solution is only weakly acidic, and this

is followed by the addition of potassium ferrocyanide, K4[Fe(CN)6], solution. The dark

blue solid that appears when iron (III) is present is a dye known as Prussian blue.

4 Fe3+ (*aq*) + 3 K4[Fe(CN)6] (*aq*) Fe4[Fe(CN)6]3 (*s*, blue) + 12 K+ **Eq. 5**

A suspension of this compound is used in some blue inks.

The presence of the cobalt ion, which now remains in the decanted supernatant

solution, can be confirmed in a simple test. The basic solution is made strongly acidic

with the addition of hydrochloric acid. Addition of a solution of potassium nitrite,

KNO2, will produce an insoluble yellow compound, potassium hexanitritocobaltate (III).

Co2+ (*aq*) + 7 NO2

– (*aq*) + 3 K+ (*aq*) + 2 H+ (*aq*) →

NO (*g*) + H2O (*l*) + K3[Co(NO2)6] (*s*, yellow) **Eq. 6**

The reaction in Eq. 6 produces nitric oxide, NO, which is a colorless gas. Nitric oxide

reacts with oxygen in the air to produce nitrogen dioxide, NO2, which may be visible as a

red-brown gas.

2 NO (*g*, colorless) + O2 (*g*) →2 NO2 (*g*, red-brown) **Eq. 7**

6

**Procedure**

Make a table in your notebook similar to that shown on page 9 *before* coming to

lab. Enter all your observations in this table.

You will dispense 2 mL of a solution that contains Ag+ **(toxic)**, Fe3+ and Co2+ into

a test tube. To use the bottletop dispenser, refer to the picture attached to the bottle.

Raise the piston slowly and evenly to the stop. Place a 13x100 mm test tube under the

discharge tube, then press down slowly and evenly on the piston. Never touch the

volume-setting knob on the side of the piston casing!

Transfer 15 drops of the solution in the test tube to a smaller, 10x75 mm, test tube

using a medicine dropper. Add 6 drops of 6 M HCl solution **(corrosive)** to the 15 drops

of the cation solution to bring about precipitation. Be sure to stir (with a clean stirring

rod) the contents of the test tube. Centrifuge the test tube for 2 minutes. Add one drop of

6 M HCl to the test tube and carefully observe the supernatant. If more precipitate is

formed upon this addition, add another drop or two of HCl and centrifuge again. Re-test

the solution for complete precipitation.

Confirming the presence of Ag+ ion

When it has been determined that precipitation of silver chloride is complete,

decant the supernatant into a clean test tube, label it and set it aside. Wash the precipitate

that remains in the test tube by adding 10-15 drops of water to it. Stir the precipitate well

and centrifuge the test tube. Decant and discard the supernatant. Repeat this procedure

to wash the precipitate one more time. Add 8 drops of 6 M NH3 solution **(corrosive,**

**irritant, strong fumes)** to the washed precipitate and stir well. Record your

observations. Add 6 M HNO3 solution **(corrosive, strong oxidant)** with mixing until the

solution is acidic when tested with litmus paper. Record your observations.

**Important!** Discard all precipitates and solutions that you suspect contain silver into the

**Laboratory Byproducts Jar** labeled “Silver”. Do not dispose of silver down the sink!

Separating and confirming the presence of Fe3+ ion

Add a sufficient amount of 6 M NH3 solution to the supernatant that was set aside

earlier until the solution is basic when tested with litmus paper. **Stir well and be sure**

**the solution is *strongly* basic!** Centrifuge the test tube and test for complete

precipitation. When it has been determined that the precipitation of iron(III) hydroxide is

complete, decant the supernatant into a clean test tube, label it and set it aside. Wash the

remaining precipitate with water. Add 10 drops of 6 M HCl to the washed precipitate.

Heat the mixture in a boiling water bath to dissolve the precipitate, if necessary. When

the precipitate has dissolved, test with litmus paper to be sure it is strongly acidic.

Separate the solution into two approximately equal portions. To one portion, add 3 drops

of 0.1 M KSCN solution and record your observations. To the other portion, add

6 M NH3 until the solution, which was strongly acidic, now tests only weakly acidic. If

the solution becomes basic, add 6 M acetic acid solution dropwise until it is weakly

acidic. Add 3 drops of 0.1 M K4[Fe(CN)6] solution and record your observations.

Confirming the presence of Co2+ ion

To the supernatant that was set aside, add 6 M HCl until the solution tests acidic.

**In a fume hood (the gas generated is toxic!)**, add 6 drops of 6 M KNO2 solution

7

**(oxidizer, irritant)**, mix well and record your observations. When the evolution of gas

has subsided (this may require several minutes), centrifuge the test tube and discard the

supernatant so that the precipitate and its color can be clearly observed. The appearance

of a yellow precipitate confirms the presence of Co2+.

**Note:** All solutions and precipitates that do **not** contain silver may be disposed of in the

sink.

Obtain from your instructor an unknown solution that contains one or more of the

cations Ag+, Fe3+ and Co2+. Repeat the above procedure using 15 drops of this solution.

Record all your observations, then fill in the data sheet on page 11 and hand it in to your

TA before leaving the laboratory.

Wash your hands thoroughly before leaving the lab**Experiment 12: Qualitative Analysis of Cations**

*Pre-Laboratory Assignment*

The pre-lab assignment for Part A of the experiment is to complete the flow chart

and answer the question on page 10 of this document. There is **no** pre-lab

assignment for Part B.

**Objective:** To separate different cations in aqueous mixtures using selective

precipitation and to confirm their identities using chemical tests.

**Introduction**

The Eagle Art Studio and Print Shop had finally found an appropriate space to

rent near the center of town. They were able to move into a large vacant room

overlooking the baseball diamond and playground of Milford Park. However, the

location of an art studio near the park had some of the town residents worried. What if

the paints, inks and ceramic pigments that the artists used were being poured into the

sinks? Could the metallic components responsible for the colors get into the

groundwater?

The Town Council contacted the Massachusetts Water Resource Authority, which

scheduled tests to be run on the water coming out of the studio. The owners of the shop

decided they should do some of their own tests on samples from the sink traps in the

building in order to determine what metallic cations their employees might be discarding

into the drains.

**Principles of the Qualitative Analysis of Cations**

The process of finding out *what* compounds are contained in a sample is called

***qualitative analysis***. The process of finding out *how much* of a compound is contained in

a sample is called ***quantitative analysis***. You have used several *quantitative* analysis

techniques, such as titration and spectrophotometry. During the next three weeks, you

will use *qualitative* analysis techniques in order to determine what metallic cations are

contained in aqueous solutions that are provided for you. These techniques will allow

you to both separate the cations in the mixture as well as to identify them.

The various salts of the cations that you will be studying have varying solubilities

in water. The differences in solubilities of these salts can be exploited in such a way as to

allow for separation of the cations. As an example, let’s examine the cations calcium,

Ca2+, and sodium, Na+. Calcium chloride is readily soluble in water, while calcium

hydroxide is highly insoluble in water. By contrast, sodium chloride and sodium

hydroxide are both readily soluble in water. An aqueous solution which contains a

mixture of calcium chloride and sodium chloride can be treated with an aqueous solution

that contains hydroxide ions. The result of such treatment will be the formation of a solid

precipitate that is composed of insoluble calcium hydroxide. The sodium hydroxide, on

the other hand, remains dissolved in the water. The solid material that contains the

calcium ions can be separated from the aqueous solution containing the sodium ions

using a technique such as filtration.

In summary, the addition of an appropriate chemical reagent to an aqueous

mixture of cations can selectively cause one or more of the cations to form a solid

precipitate while one or more of the cations will remain dissolved in the water, thus

2

allowing for separation. (Pages 749-754 in Tro also discuss principles involved in

qualitative analysis.)

**General Procedures for the Qualitative Analysis of Cations**

*Avoiding Contamination*

As you follow the procedures for separating and identifying the cations in a

mixture, it will be extremely important to avoid contamination of the samples and

chemical reagents at all times. The presence of a contaminant that contains a cation will

lead to a false positive result; therefore, it is critical that all glassware be thoroughly

cleaned before it is used and should remain clean throughout the procedure. Laying a

glass stirring rod on a dirty lab bench, for instance, could lead to contamination.

Touching the tip of a medicine dropper to the side of a test tube could cause contaminants

to be picked up and transferred to another solution. In addition, all water used for these

procedures must come from the plastic, white faucets in the lab that deliver de-ionized

water. Tap water from the regular faucets contains a wide variety of ions and could result

in misleading observations.

*Equipment and Chemicals*

The tests that you will perform to identify the cations after they have been

separated require only very small amounts of sample. Therefore, you will work with the

smallest size test tubes available (10 x 75 mm), thin glass stirring rods and medicine

droppers. Rather than measuring volumes of liquids with a graduated cylinder, it will be

easier to simply count the number of drops of liquid dispensed from a medicine dropper.

In general, it is safe to assume that *20 drops from a medicine dropper is equivalent to*

*1 mL of solution*. You will usually be told exactly how many drops to add in any given

step of the procedure. As mentioned previously, it is very important that the medicine

droppers **never** become contaminated, for instance, by allowing the tip to touch either the

surface of a solution or the side of a test tube.

The chemical reagents for the qualitative analysis procedures are aqueous

solutions that are contained in dropper bottles. The caps of these bottles are labeled. Do

not put the wrong dropper into a bottle, or the entire contents of the bottle will become

contaminated! When you have finished using the bottle, screw the cap back on *tightly*. If

the cap is not on tight, the next person to grab it by the dropper will knock the bottle over.

In addition, some of the water will evaporate if the cap is not on tight, and this will alter

the concentration of the solution.

*Mixing*

After a reagent has been added to a solution in a test tube, it is very important that

the solutions are stirred together thoroughly. Reactions cannot proceed to completion

unless the reactants come into intimate contact with each other. Use a *thin* stirring rod to

mix the liquids so that the contents of the test tube do not overflow. Of course, the

stirring rod must be rinsed well with de-ionized water before being used.

*Checking Acidity/Basicity*

In many cases during the separation of cations, an acid or base solution is added

to a sample until the pH of the solution becomes either acidic or basic. In these instances,

litmus paper is used to monitor the pH. A drop of the solution being tested is removed

from the test tube using a glass stirring rod. The rod is touched to the litmus paper, and

3

the color of the paper indicates whether the pH is basic (blue) or acidic (red). The litmus

paper must never be placed directly into the solution! It is possible to use litmus paper to

observe if a solution is weakly acidic or basic as opposed to strongly acidic or basic. A

strong acid or base will turn litmus paper a more intense color than will a weak acid or

base.

*Forming, Separating and Washing Precipitates*

When an appropriate chemical reagent is added to a solution containing a mixture

of cations, a precipitate will form that is composed of the insoluble salt(s) of one or more

of the cations. This solid precipitate can be separated from the aqueous solution, which

contains the soluble salt(s) of the remaining cations, by filtration; however, a more

convenient technique for the separation of a solid from a liquid is centrifugation. A test

tube containing the mixture is placed in a centrifuge, which spins the mixture at a very

high speed. The resulting centrifugal force packs the solid material tightly into the

bottom of the test tube. The liquid supernatant can then be easily poured away, or

*decanted*, from the solid. Read about Using a Centrifuge in TECH Section VI.

Before the liquid supernatant is decanted from the solid material, it is a good idea

to check for complete precipitation. After centrifuging the mixture, add one or two more

drops of the reagent which caused precipitation to occur. Watch the supernatant carefully

to see if more precipitate forms. If no more precipitate forms, then precipitation is

complete and the supernatant may be poured off. If more solid does appear in the

supernatant, add another drop or two of the reagent solution, thoroughly stir the contents

of the test tube, and place it back in the centrifuge for two minutes. The process of

checking for complete precipitation should continue until no solid appears in the

supernatant upon addition of the reagent.

After the liquid has been decanted from the solid, a small amount of this solution

will remain behind in the test tube with the solid. In order to completely remove this

liquid and any contaminants that it contains, the precipitate is washed with water. Ten to

fifteen drops of water are added to the test tube, and the mixture of solid and liquid is

thoroughly stirred with a glass rod. The test tube is place in a centrifuge for two minutes,

then the water is decanted away from the solid and may be disposed of down the drain.

Solids are usually washed two times before proceeding to the next step in the procedure.

*Heating Solutions*

Occasionally, a step in a qualitative analysis procedure will require that a solution

or mixture be heated. A water bath usually provides a high enough temperature. Place

about 150 mL of water in a 250 mL beaker and heat it on a hot plate. A metal *beaker*

*cover* with four holes in it is available in your drawer. This metal plate can be placed on

top of the beaker, and 10 x 75 mm test tubes can be inserted into the holes such that the

bottom of the test tube is positioned in the middle of the boiling water. It can take some

time for the water to reach the boiling point, so if you know you will require a water bath

at some point in the procedure, you should set the water on a hot plate at the beginning of

the lab period.

*Labeling*

During the qualitative analysis procedures, you will be manipulating a large

number of test tubes with a variety of contents. It is vital that everything be clearly and

properly labeled. Solutions and solids can be inadvertently discarded if test tubes do not

4

have accurate labels. Also, before you place one of your test tubes in the centrifuge with

other students’ test tubes, you must label it with your name.

*Laboratory Notebook*

As always, you must record very complete and descriptive observations in your

lab notebook throughout the qualitative analysis procedures. You might find it useful to

organize your observations in a table. Color changes, the presence or absence of

cloudiness and the formation of bubbles are all relevant observations that must be

carefully noted. You should record the color of solutions *before* they are added to each

other, as well as what happens after they are mixed together. Remember that there is a

difference between the terms *clear* and *colorless*. To say that a liquid is “clear” indicates

that no solid material is present, while the absence of color is best described by the word

“colorless”. For instance, if two non-colored solutions are mixed together and a white

precipitate forms, the correct observation is a “colorless and cloudy” mixture.

Your TA will collect the carbon copies of your notebook pages at the end of each

of the qualitative analysis lab periods. Because you will be performing the qualitative

analyses over three lab periods, it is especially important that you record completely what

you did and what you observed in lab each day. You will need to refer to observations

from the previous lab periods in order to successfully complete the analyses.

*Hazardous Chemical Byproducts*

Some of the chemical reagents and cations that you will work with during the

qualitative analysis procedures are toxic. These materials present a hazard to the

environment and must be collected in the **Laboratory Byproducts** jars. Those

chemicals that are not hazardous may be safely poured down the drain. Read carefully

the instructions provided for each experiment, and listen to your instructor’s pre-lab talk

to learn which materials may be disposed of in the sink and which must be collected in a

Byproducts jar. Ask your TA if you have any questions regarding the proper disposal of

a chemical.

*Safety Precautions*

The standard safety rules must be followed when carrying out the qualitative

analysis procedures. You must wear both a lab apron and chemical splash goggles.

Some of the reactions that occur will generate hazardous fumes such as ammonia, so it is

prudent to work in the fume hood whenever possible. Read the labels of reagent bottles

carefully to be sure you have chosen the right chemical and the right concentration.

**The Analyses**

In the first week of the qualitative analysis sequence, you will be given explicit

instructions to follow in order to separate the cations Ag+, Fe3+ and Co2+ and confirm

their presence (Part A). In the second and third weeks, you will have to devise your own

scheme for separating the cations ZrO2+, Ni2+, Pb2+ and Al3+ (Part B). In both Parts A

and B, you will first be provided with a solution that contains all of the cations in

question. After you have successfully followed the procedure to separate and confirm

their presence, you will be given an “unknown” solution that contains one or more of the

indicated cations. By following the same procedure that you used for the “known”

solution, you will be able to identify which of the cations are present in the “unknown”

solution.

5

**Part A. Analyzing Solutions for Silver (I), Iron (III) and Cobalt (II) Ions**

The first step in the separation of these three cations involves the precipitation of

the silver ion as the insoluble silver chloride salt. This precipitation is accomplished

simply through the addition of hydrochloric acid.

Ag+ (*aq*) + HCl (*aq*) AgCl (*s*) + H+ (*aq*) **Eq. 1**

Since neither iron (III) nor cobalt (II) forms an insoluble chloride salt, the silver can then

be separated from the other two cations by centrifuging the test tube and decanting the

supernatant. A test is next performed to confirm the presence of silver in the precipitate

that remains in the test tube. First, ammonia is added, which results in dissolution of the

silver (I) compound.

AgCl (*s*) + 2 NH3 (*aq*) Ag(NH3)2

+ (*aq*) + Cl– (*aq*) **Eq. 2**

Adding nitric acid will shift the equilibrium to the left as the acid reacts with the

ammonia, NH3, causing the silver ion to re-precipitate as silver chloride.

The supernatant that was decanted earlier contains both Fe3+ and Co2+. Addition

of ammonia to this solution causes the iron (III) ion to form an insoluble hydroxide and

precipitate out of solution.

Fe3+ (*aq*) + 3 NH3 (*aq*) + 3 H2O (*l*) Fe(OH)3 (*s*) + 3 NH4

+ (*aq*) **Eq. 3**

Centrifugation and decantation leaves Fe(OH)3 solid which can be dissolved in hot

hydrochloric acid. There are two confirmation tests for iron (III), and you will perform

both. In the first, addition of potassium thiocyanate solution produces a red-brown color

if Fe3+ is present.

Fe3+ (*aq*) + SCN– (*aq*) Fe(SCN)2+ (*aq*, red-brown) **Eq. 4**

In the second test, ammonia is first added until the solution is only weakly acidic, and this

is followed by the addition of potassium ferrocyanide, K4[Fe(CN)6], solution. The dark

blue solid that appears when iron (III) is present is a dye known as Prussian blue.

4 Fe3+ (*aq*) + 3 K4[Fe(CN)6] (*aq*) Fe4[Fe(CN)6]3 (*s*, blue) + 12 K+ **Eq. 5**

A suspension of this compound is used in some blue inks.

The presence of the cobalt ion, which now remains in the decanted supernatant

solution, can be confirmed in a simple test. The basic solution is made strongly acidic

with the addition of hydrochloric acid. Addition of a solution of potassium nitrite,

KNO2, will produce an insoluble yellow compound, potassium hexanitritocobaltate (III).

Co2+ (*aq*) + 7 NO2

– (*aq*) + 3 K+ (*aq*) + 2 H+ (*aq*) →

NO (*g*) + H2O (*l*) + K3[Co(NO2)6] (*s*, yellow) **Eq. 6**

The reaction in Eq. 6 produces nitric oxide, NO, which is a colorless gas. Nitric oxide

reacts with oxygen in the air to produce nitrogen dioxide, NO2, which may be visible as a

red-brown gas.

2 NO (*g*, colorless) + O2 (*g*) →2 NO2 (*g*, red-brown) **Eq. 7**

6

**Procedure**

Make a table in your notebook similar to that shown on page 9 *before* coming to

lab. Enter all your observations in this table.

You will dispense 2 mL of a solution that contains Ag+ **(toxic)**, Fe3+ and Co2+ into

a test tube. To use the bottletop dispenser, refer to the picture attached to the bottle.

Raise the piston slowly and evenly to the stop. Place a 13x100 mm test tube under the

discharge tube, then press down slowly and evenly on the piston. Never touch the

volume-setting knob on the side of the piston casing!

Transfer 15 drops of the solution in the test tube to a smaller, 10x75 mm, test tube

using a medicine dropper. Add 6 drops of 6 M HCl solution **(corrosive)** to the 15 drops

of the cation solution to bring about precipitation. Be sure to stir (with a clean stirring

rod) the contents of the test tube. Centrifuge the test tube for 2 minutes. Add one drop of

6 M HCl to the test tube and carefully observe the supernatant. If more precipitate is

formed upon this addition, add another drop or two of HCl and centrifuge again. Re-test

the solution for complete precipitation.

Confirming the presence of Ag+ ion

When it has been determined that precipitation of silver chloride is complete,

decant the supernatant into a clean test tube, label it and set it aside. Wash the precipitate

that remains in the test tube by adding 10-15 drops of water to it. Stir the precipitate well

and centrifuge the test tube. Decant and discard the supernatant. Repeat this procedure

to wash the precipitate one more time. Add 8 drops of 6 M NH3 solution **(corrosive,**

**irritant, strong fumes)** to the washed precipitate and stir well. Record your

observations. Add 6 M HNO3 solution **(corrosive, strong oxidant)** with mixing until the

solution is acidic when tested with litmus paper. Record your observations.

**Important!** Discard all precipitates and solutions that you suspect contain silver into the

**Laboratory Byproducts Jar** labeled “Silver”. Do not dispose of silver down the sink!

Separating and confirming the presence of Fe3+ ion

Add a sufficient amount of 6 M NH3 solution to the supernatant that was set aside

earlier until the solution is basic when tested with litmus paper. **Stir well and be sure**

**the solution is *strongly* basic!** Centrifuge the test tube and test for complete

precipitation. When it has been determined that the precipitation of iron(III) hydroxide is

complete, decant the supernatant into a clean test tube, label it and set it aside. Wash the

remaining precipitate with water. Add 10 drops of 6 M HCl to the washed precipitate.

Heat the mixture in a boiling water bath to dissolve the precipitate, if necessary. When

the precipitate has dissolved, test with litmus paper to be sure it is strongly acidic.

Separate the solution into two approximately equal portions. To one portion, add 3 drops

of 0.1 M KSCN solution and record your observations. To the other portion, add

6 M NH3 until the solution, which was strongly acidic, now tests only weakly acidic. If

the solution becomes basic, add 6 M acetic acid solution dropwise until it is weakly

acidic. Add 3 drops of 0.1 M K4[Fe(CN)6] solution and record your observations.

Confirming the presence of Co2+ ion

To the supernatant that was set aside, add 6 M HCl until the solution tests acidic.

**In a fume hood (the gas generated is toxic!)**, add 6 drops of 6 M KNO2 solution

7

**(oxidizer, irritant)**, mix well and record your observations. When the evolution of gas

has subsided (this may require several minutes), centrifuge the test tube and discard the

supernatant so that the precipitate and its color can be clearly observed. The appearance

of a yellow precipitate confirms the presence of Co2+.

**Note:** All solutions and precipitates that do **not** contain silver may be disposed of in the

sink.

Obtain from your instructor an unknown solution that contains one or more of the

cations Ag+, Fe3+ and Co2+. Repeat the above procedure using 15 drops of this solution.

Record all your observations, then fill in the data sheet on page 11 and hand it in to your

TA before leaving the laboratory.

Wash your hands thoroughly before leaving the lab