

# Experiment 3

## *Environmental Forensics*



## The Task

The goal of this experiment is to identify the anion and the cation present in an inorganic compound.

## Skills

At the end of the laboratory you should be able to:

- test for carbonates,
- distinguish between different halides,
- test for the presence of  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ .

## Other Outcomes

- You will learn how to carry out a flame test.
- You will gain practice in the use of semi-micro techniques and qualitative analysis.

## The Assessment

You will be assessed on your ability to identify the presence (or absence) of a particular metal ion by the use of a flame test. See Skill 12.

## Introduction

Analytical chemistry forms an important part of environmental science. As you should have already seen in E12, the growth of plants depends to a large extent on the ions present, which determine the soil pH and hence the chemical state of nutrients within the soil. An analysis of the ions present in soil thus forms an important part of its chemical characterisation. But plants are not the only form of life affected by the ions present within their environment. The health of animals, including humans, is also very dependent on the ions to which they are exposed. There are, for example, many metal ions which are essential to our existence (*e.g.*  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) because of crucial roles they play in our metabolism or other physiological processes, such as respiration, muscle contraction, nerve impulse propagation, *etc.*

Unfortunately other metal ions, because of their similar ionic radii or chemical properties, can often compete with these biologically essential ions, disrupting the physiological processes with which they are involved and leading to a variety of pathological conditions, and even cancer. Some of the most toxic metal ions include  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{As}^{3+}$ . Lead poisoning, for example, results in an inhibition of the biosynthesis of the haem of haemoglobin, which is responsible for oxygen transport in our bloodstream. Even relatively low levels of exposure to  $\text{Pb}^{2+}$  thus lead to anaemia, and, in the case of children, to an impairment of brain development. Even essential metal ions such as  $\text{Cu}^{2+}$  can be toxic when the level rises beyond a certain level. Therefore, our bodies have complex mechanisms, often involving ion pumps, to maintain the level of the essential metal ions at the appropriate physiological level. Because of the crucial impact of both essential and toxic metals on the health of both plants and animals, it is important to have means of analysing their concentrations in the environment, *e.g.* to avoid dangers to human health as a result of industrial pollution.

In this experiment you will explore a range of simple chemical tests for different anions and cations. Although these tests are not all appropriate for determining concentrations of these ions (nowadays this would mostly be done via spectroscopic methods), they allow a relatively quick and simple detection of the type of anion or cation in a sample.

### ***Colour and Solubility***

Before doing any tests on the reactivity of an inorganic compound, clues to its possible identity can be obtained simply by observing its colour, testing its solubility in water and observing the colour of its solution (if applicable). Table 1 lists the colours of common forms of a variety of inorganic compounds. Note, however, that the colour can vary considerably with the state of hydration. For example, anhydrous  $\text{CoCl}_2$  is actually blue, but the table refers to the more common hydrated form  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , which is red. Compounds that are unstable or do not exist are indicated with a dash. Table 2 lists the colours of different metal ions in solution. The solubility in water of common inorganic compounds is summarised in Table 3.

Colour and solubility are, however, generally insufficient to identify a compound with certainty, rather they provide supporting evidence for ion tests.

## E3-4

Table 1: Colours of Solid Compounds

	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	OH <sup>-</sup>	O <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	
Ag <sup>+</sup>	white	yellow	yellow	brown	brown	white	white	white	
Cu <sup>2+</sup>	green	black	–	blue	black	blue	blue	green	
Pb <sup>2+</sup>	white	white	yellow	white	yellow	white	white	white	
Sn <sup>2+</sup>	white	yellow	orange	white	black	white	white	–	
Ni <sup>2+</sup>	green	green	black	green	black	green	green	green	
Co <sup>2+</sup>	red	red	black	pink	black	red	red	red	
Fe <sup>3+</sup>	brown	red	–	brown	red	yellow	grey	–	
Fe <sup>2+</sup>	green	grn-yel	grey	green	black	green	green	green	
Cr <sup>3+</sup>	violet	green	black	blue/grn	black	violet	violet	–	
Cd <sup>2+</sup>	white	yellow	grn/yell	white	brown	white	white	white	
Zn <sup>2+</sup>	white								
Mn <sup>2+</sup>	pink	pink	pink	pink	grey	pink	pink	pink	
Al <sup>3+</sup>	white								–
Mg <sup>2+</sup>									
Ca <sup>2+</sup>									
Sr <sup>2+</sup>									
Ba <sup>2+</sup>									
Na <sup>+</sup>									
K <sup>+</sup>									
NH <sub>4</sub> <sup>+</sup>									–

Table 2: Colours of Some Ions in Solution.

Cation	Colour of ion in aqueous solution
Cr <sup>3+</sup> (aq)	green or blue or grey
Mn <sup>2+</sup> (aq)	colourless to very pale pink
Fe <sup>2+</sup> (aq)	pale green (colourless in very dilute solution)
Fe <sup>3+</sup> (aq)	pale violet, but yellow in the presence of most anions
Co <sup>2+</sup> (aq)	Pink
Ni <sup>2+</sup> (aq)	Green
Cu <sup>2+</sup> (aq)	blue or green

Table 3: Aqueous Solubility of Inorganic Compounds

ANION	BEHAVIOUR WITH COMMON CATIONS		
	USUAL	EXCEPTIONAL	SLIGHTLY SOLUBLE
F <sup>-</sup>	soluble	except Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , Mn <sup>2+</sup> , Pb <sup>2+</sup>	Al <sup>3+</sup>
Cl <sup>-</sup>	soluble	except Ag <sup>+</sup> , Hg <sub>2</sub> <sup>2+</sup>	Pb <sup>2+</sup>
Br <sup>-</sup>	soluble	except Ag <sup>+</sup> , Hg <sub>2</sub> <sup>2+</sup>	Hg <sup>2+</sup> , Pb <sup>2+</sup>
I <sup>-</sup>	soluble	except Ag <sup>+</sup> , Hg <sub>2</sub> <sup>2+</sup> , Hg <sup>2+</sup> , Pb <sup>2+</sup>	
SO <sub>4</sub> <sup>2-</sup>	soluble	except Sr <sup>2+</sup> , Ba <sup>2+</sup> , Hg <sub>2</sub> <sup>2+</sup> , Pb <sup>2+</sup>	Ca <sup>2+</sup> , Ag <sup>+</sup>
NO <sub>3</sub> <sup>-</sup>	soluble		
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	soluble		Ag <sup>+</sup> , Hg <sub>2</sub> <sup>2+</sup>
OH <sup>-</sup>	insoluble	except Na <sup>+</sup> , K <sup>+</sup> , Ba <sup>2+</sup>	Ca <sup>2+</sup> , Sr <sup>2+</sup>
O <sup>2-</sup>	insoluble	except Na <sup>+</sup> , K <sup>+</sup> , Ba <sup>2+</sup>	Ca <sup>2+</sup> , Sr <sup>2+</sup>
SO <sub>3</sub> <sup>2-</sup>	insoluble	except Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Mg <sup>2+</sup>	
PO <sub>4</sub> <sup>3-</sup>	insoluble	except Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	
CO <sub>3</sub> <sup>2-</sup>	insoluble	except Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	insoluble	except Na <sup>+</sup> , K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>
S <sup>2-</sup>	insoluble	except Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup>	

**Anion Tests**

The anion tests you will carry out are as follows:

T<sub>An1</sub> Test for carbonates

T<sub>An2</sub> Tests for halides

*T<sub>An1</sub>: Test for carbonates*

A sample of the solid is tested with nitric acid solution. The evolution of an odourless gas, as evidenced by bubbling or fizzing of the solid, indicates an acid/base reaction of a carbonate.

*T<sub>An2</sub>: Test for halides*

The solid is dissolved in nitric acid and tested with silver nitrate solution. If a white or creamish coloured precipitate forms, the presence of a halide is indicated.

If the above test is positive, a further test must be undertaken to determine **which** halide is present. The solid unknown is treated with manganese dioxide in the presence of sulfuric acid. Evolution of a pale green to colourless gas (Cl<sub>2</sub>) indicates chloride, a brown gas (Br<sub>2</sub>) indicates bromide and a violet gas (I<sub>2</sub>) indicates iodide.

**Cation Tests**

The cation tests you will carry out are as follows:

T<sub>Cat1</sub> Test for Ag<sup>+</sup> and Pb<sup>2+</sup> as insoluble chlorides

T<sub>Cat2</sub> Tests for Cd<sup>2+</sup>, Cu<sup>2+</sup> and Sn<sup>2+</sup> as insoluble sulfides (acidic conditions)

T<sub>Cat3</sub> Test for Fe<sup>3+</sup>, Cr<sup>3+</sup> and Al<sup>3+</sup> as insoluble hydroxides

T<sub>Cat4</sub> Test for Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> as insoluble sulfides (basic conditions)

T<sub>Cat5</sub> Test for Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> as insoluble carbonates

*T<sub>Cat1</sub>: Test for Ag<sup>+</sup> and Pb<sup>2+</sup>*

The solid is dissolved in nitric acid and hydrochloric acid added. The presence of a white precipitate indicates the presence of Pb<sup>2+</sup> or Ag<sup>+</sup>.

To identify which cation is present, just leave the precipitate to stand for a few minutes in direct sunlight. AgCl will go a distinct purple colour as it decomposes to metallic silver (this was the basis of the photographic industry before digital cameras), whilst PbCl<sub>2</sub> will undergo no change.

*T<sub>Cat2</sub>: Test for Cd<sup>2+</sup>, Cu<sup>2+</sup> and Sn<sup>2+</sup>*

Aqueous H<sub>2</sub>S is generated under acid conditions *in situ* from thioacetamide. If a precipitate forms, then either Cd<sup>2+</sup> (bright yellow), Sn<sup>2+</sup> (brown) or Cu<sup>2+</sup> (black from a blue or green solution) is present.

*T<sub>Cat3</sub>: Test for Fe<sup>3+</sup>, Cr<sup>3+</sup> and Al<sup>3+</sup>*

The sample is dissolved in nitric acid and heated for several minutes. Solid NH<sub>4</sub>Cl and 16 M NH<sub>3</sub> is then added. A brown precipitate indicates the presence of Fe<sup>3+</sup> in the solution (although it may have initially been Fe<sup>2+</sup> or Fe<sup>3+</sup> in the solid), a grey or green precipitate indicates Cr<sup>3+</sup> and a white precipitate indicates Al<sup>3+</sup>.

If iron is detected, a further test is required to determine its oxidation state in the original compound. Fe<sup>3+</sup> forms a blood red colour with KSCN solution, whilst Fe<sup>2+</sup> forms a pink colour with a solution of 2,2'-bipyridine in ethanol.

*T<sub>Cat4</sub>: Test for Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>*

The unknown is dissolved in hydrochloric acid and solid NH<sub>4</sub>Cl and 16 M NH<sub>3</sub> is added. Aqueous H<sub>2</sub>S is generated under basic conditions *in situ* from thioacetamide. If a precipitate forms, then either Ni<sup>2+</sup> (black from a blue-violet solution), Co<sup>2+</sup> (black from a brown solution), Zn<sup>2+</sup> (white), or Mn<sup>2+</sup> (peach, orange-pink) is present.

*T<sub>Cat5</sub>: Test for Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup> and Mg<sup>2+</sup>*

The unknown is dissolved in water or acid and sodium carbonate solution added. A white precipitate indicates the presence of Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, or Ba<sup>2+</sup>.

To identify the specific cation present, a flame test is performed. No colour (or yellow due to Na<sup>+</sup> contaminant) indicates Mg<sup>2+</sup>, dull (brick) red indicates Ca<sup>2+</sup>, crimson indicates Sr<sup>2+</sup> and pale green indicates Ba<sup>2+</sup>.

### Flow Charts

The anion and cation tests described have been based on a process of elimination. For example, both  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  will give precipitates under the conditions described in  $T_{\text{Cat}2}$ . Similarly, all of the cations will give precipitates when sodium carbonate is added ( $T_{\text{Cat}5}$ ). Because of this, **it is absolutely essential that both the anion and the cation tests are carried out in a strict sequential order**. Once the anion or cation has been identified, there is no point in carrying out the subsequent tests - indeed, they will most likely give you a false positive (*i.e.* a positive result that leads you towards an incorrect conclusion). The order of the tests can be summarised in flow charts, as shown below for anions and on the next page for cations.

### Key to the flow charts.

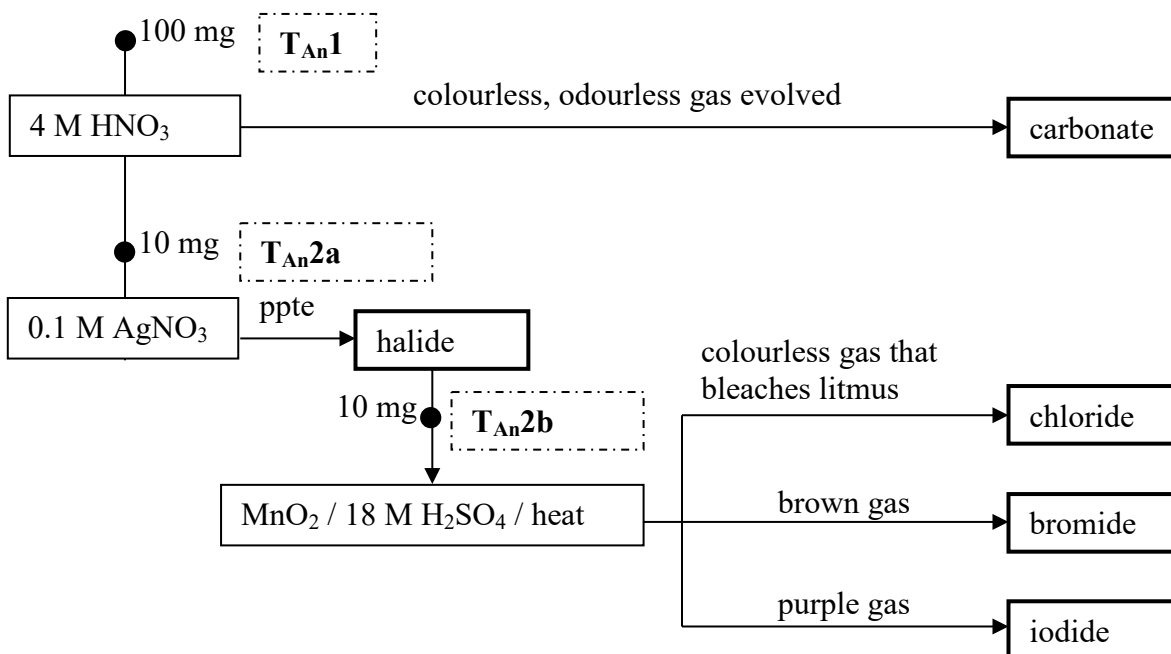
- Take a new sample of solid unknown - the amount is indicated.

   The name of the Test as shown in the text.

   The reagent used.

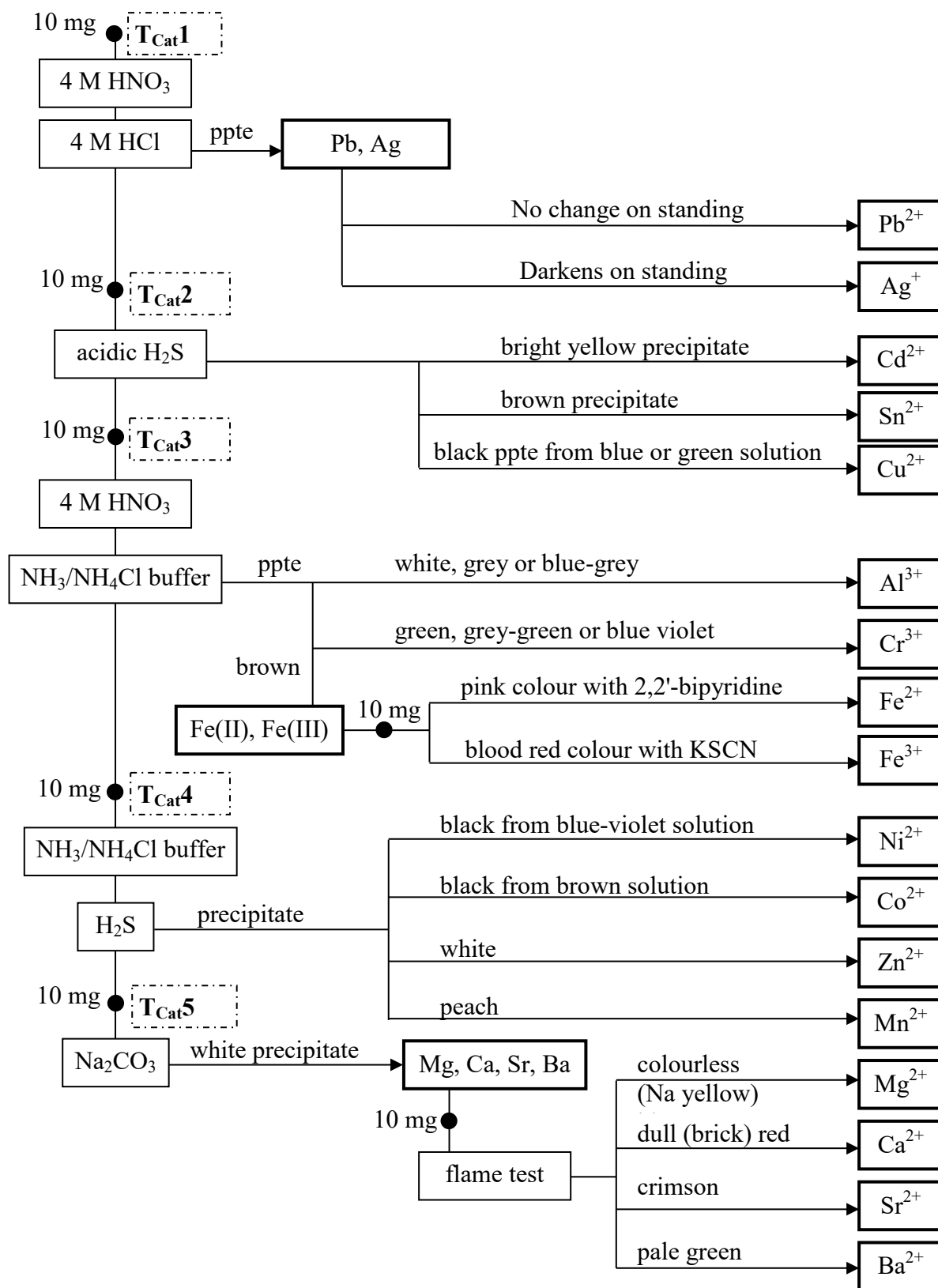
   The ion identified.

### Anion Flow Chart





## Cation Flow Chart



## Safety

### *Chemical Hazard Identification*

**4 M nitric acid** – corrosive – irritant. Avoid eye or skin contact.

**0.4 M hydrochloric acid** – non-hazardous. Avoid eye or skin contact or inhalation.

**4 M hydrochloric acid** – corrosive – irritant. Avoid eye or skin contact or inhalation.

**10 M hydrochloric acid** – corrosive, irritant. Avoid eye or skin contact or inhalation.

**18 M sulfuric acid** – corrosive – irritant. Avoid eye or skin contact.

**16 M ammonia** – hazardous – irritant. Avoid eye or skin contact and inhalation.

**manganese dioxide** – hazardous. Avoid eye or skin contact and inhalation.

**chlorine gas** – hazardous – toxic – irritant. Avoid eye or skin contact and inhalation.

**bromine gas** – hazardous – toxic – irritant. Avoid eye or skin contact and inhalation.

**iodine gas** – hazardous – toxic – irritant. Avoid eye or skin contact and inhalation.

**thioacetamide solution** – hazardous – toxic – irritant. Avoid eye or skin contact.

**hydrogen sulfide gas** – hazardous – toxic – irritant. Avoid eye or skin contact and inhalation.

**2,2'-bipyridine** - toxic – irritant. Avoid eye or skin contact.

**potassium thiocyanate** – toxic – irritant. Avoid eye or skin contact and inhalation.

**ammonium chloride** – hazardous – irritant. Avoid eye or skin contact and inhalation.

**1 M sodium carbonate solution** - non-hazardous

**0.1 M silver nitrate** – irritant. Avoid eye or skin contact and inhalation.

**unknown** - must be treated as hazardous. Avoid eye or skin contact and inhalation.

### *Risk Assessment and Control*

Moderate risk.

Semi-micro test tubes must never be heated in a direct flame, lest the solution boils and erupts explosively. They must be placed in a beaker of boiling water instead.

Bunsen burners present fire and burn hazards - take care.

### *Waste Disposal*

Heavy metal residues must be discarded in the appropriate residue containers in the fume hoods. (Unknowns should be treated as heavy metals.) All thioacetamide residues must go in the appropriate residue container in the fume hoods.

## Experimental

*This experiment is to be carried out individually.*

You are expected to identify 2 separate unknown salts. They will be issued to you by your Demonstrator. Complete all the tests for one compound before you begin work on the second.

### Part A Colour and Solubility

- (A1) Place 0.1 g of the solid unknown in a semi-micro tube. Do not do any weighing - estimate all weights based on the tubes at the front of the lab.
- (A2) Add 0.5 mL (about 10 drops) of water.
- (A3) Mix by shaking or stirring. If the solid doesn't dissolve, heat the tube in a boiling water-bath for 3 minutes. **Record your observations in your logbook**, *i.e.* is the compound soluble, slightly soluble, insoluble or soluble on heating.
- (A4) Inspect the solid compound and its solution. **Record the colour of both in your logbook.**

***For your logbook:***

*Based on the solubility of the compound, its colour and the colour of its solution, make a guess as to what the formula of the compound might be or definitely won't be.*

### Part B Anion Tests

Test for carbonates (T<sub>An</sub>1)

- (B1) Place 0.1 g (again estimate the weight based on the tubes at the front of the lab) of the solid unknown in a semi-micro tube.
- (B2) Add 0.5 mL of 4 M HNO<sub>3</sub>. **Record your observations in your logbook.**

***For your logbook:***

*Do you have any evidence that the unknown is a carbonate?*

Test for halides (T<sub>An</sub>2a)

- (B3) Place 10 mg (again, estimated weight) of the solid unknown in a semi-micro tube.
- (B4) Add 0.5 mL of 4 M HNO<sub>3</sub> and heat the solution in the water bath until clear (but not necessarily colourless). Then add 1 drop of 0.1 M AgNO<sub>3</sub> and **record your observations in your logbook.**

*Note:* If you observe a brown solution, a dark precipitate or a brown gas in step (B4), the procedure needs to be modified to reduce the NO<sub>3</sub><sup>-</sup> concentration. Take a new sample of the solid (10 mg) and dissolve in 0.5 mL of water and then add 1 drop of 4 M HNO<sub>3</sub>. Heat, add the AgNO<sub>3</sub> and record your observations as above.

- (B5) Take a new semi-micro tube and repeat step (B4, but using deionised water instead of HNO<sub>3</sub>. This is a blank test for comparison with the result found from step (B4).

***For your logbook:***

*Do you have any evidence that the unknown is a halide?*

Test for specific identification of a halide (T<sub>An</sub>2b)

**N.B. Only perform this test if T<sub>An</sub>2a is positive.**

- (B6) Place 10 mg of the solid in a dry semi-micro tube.
- (B7) Add 10 mg of MnO<sub>2</sub> to the same tube.
- (B8) Support the tube in a holder and carefully add 3 drops of 18 M H<sub>2</sub>SO<sub>4</sub>.
- (B9) Heat the tube gently in a water bath. **Record your observations in your logbook.**
- (B10) If you suspect that chlorine gas may have been evolved, test whether the gas is able to bleach moist litmus paper (a characteristic reaction of Cl<sub>2</sub>). Record your observations in your logbook.

***For your logbook:***

*Do you have any evidence that the unknown is a chloride, bromide or iodide?*

**Part C Cation Tests**

Test for Ag<sup>+</sup> and Pb<sup>2+</sup> (T<sub>Cat</sub>1)

- (C1) Place 10 mg of the solid unknown in a semi-micro tube.
- (C2) Add 0.5 mL of 4 M HNO<sub>3</sub>.
- (C3) Dissolve the solid, if necessary by warming. Then cool.
- (C4) Add 1 drop of 4 M HCl.
- (C5) If a precipitate is formed, allow it to stand for a few minutes. **Record your observations in your logbook.**

***For your logbook:***

*Do you have any evidence that the unknown could contain Ag<sup>+</sup> or Pb<sup>2+</sup>? If so, which is it?*

Test for  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Sn}^{2+}$  ( $T_{\text{Cat}2}$ )

- (C6) Place 10 mg of the solid unknown in a semi-micro tube.
- (C7) Add 0.5 mL of 0.4 M HCl and heat in a water bath.
- (C8) In a fume hood, add 10 drops of thioacetamide solution to produce  $\text{H}_2\text{S}$  and stir the resulting mixture.
- (C9) Heat in the water bath for several minutes further. Record your observations in your logbook. A very fine, pale yellow or off-white precipitate of sulfur should be ignored. This can occur when testing an unknown if it contains either  $\text{Fe}^{3+}$  ions or  $\text{NO}_3^-$  ions. Both of these ions can oxidise  $\text{H}_2\text{S}$  to elemental sulfur.

***For your logbook:***

*Do you have any evidence that the unknown could contain  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  or  $\text{Sn}^{2+}$ ?*

Test for  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Al}^{3+}$  ( $T_{\text{Cat}3}$ )

- (C10) Place 10 mg of the solid in a semi-micro tube.
- (C11) Add 0.5 mL of 4 M  $\text{HNO}_3$ , heat for 3 minutes and then cool.
- (C12) Add 0.5 g of  $\text{NH}_4\text{Cl}$  and 0.5 mL of 16 M  $\text{NH}_3$ . Mix well with a thin stirring rod. Ignore any traces of brownish precipitate, probably hydrated  $\text{MnO}_2$ . **Record your observations in your logbook.**

***For your logbook:***

*Do you have any evidence that the unknown could contain  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  or  $\text{Al}^{3+}$ ?*

*If you think that  $\text{Fe}^{3+}$  is present, design your own experiment to identify whether the unknown compound contains  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ . Hint: see the flow chart on page E13-9.*

Test for  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ( $T_{\text{Cat}4}$ )

- (C13) Place 10 mg of the solid in a large test-tube.
- (C14) Add 0.5 mL of 4 M HCl, heat sufficiently to dissolve the solid and then cool.
- (C15) Add 0.1 g of solid  $\text{NH}_4\text{Cl}$  and 0.5 mL of 16 M  $\text{NH}_3$  (fume hood) and stir well.
- (C16) Heat in a water bath and then add 15 drops of thioacetamide solution. Heat for several minutes more in fume hood. **Record your observations in your logbook.**

***For your logbook:***

*Do you have any evidence that the unknown could contain  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  or  $\text{Zn}^{2+}$ ?*

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Test for  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  (T<sub>Cat</sub>5)

- (C17) Dissolve 10 mg of the solid in 0.5 mL of water. If it doesn't dissolve, then dissolve 10 mg of solid in 0.5 mL of 0.4 M HCl instead.
- (C18) Add 5 drops of 1 M  $\text{Na}_2\text{CO}_3$ . Record your observations in your logbook.
- (C19) If you observed a precipitate, place 10 mg of the original unknown solid on a watchglass. Moisten with 10 M HCl and perform a flame test (Skill 12) on the mixture. Record your observations in your logbook.

***For your logbook:***

*Do you have any evidence that the unknown could contain  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  or  $\text{Mg}^{2+}$ ?*

### Part D Discussion

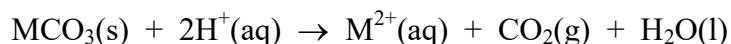
- (D1) Based on the results from all of your tests, can you identify what the unknown inorganic compound was? Does this agree with your initial guess based on its colour and solubility?
- (D2) Check with your demonstrator that you are correct.
- (D3) Record in your log book all the relevant equations for the chemical tests that led to the identification. You can find all this in the Appendix to this experiment.

## Appendix 3.1

The chemical theory behind each of the positive tests and the relevant equations are given below. You will need to refer to this section to complete Part D of the experiment.

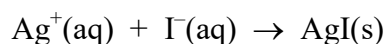
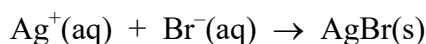
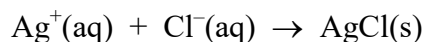
### *Test for carbonates (T<sub>An1</sub>)*

Although most carbonates are insoluble in water, all dissolve in dilute nitric acid.



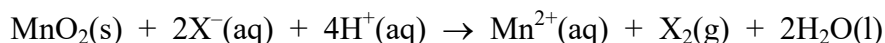
### *Test for halides (T<sub>An2a</sub>)*

The solid is dissolved in nitric acid and tested with silver nitrate solution. If a white or cream coloured precipitate forms, the presence of a halide is indicated.



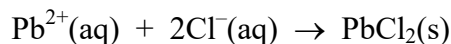
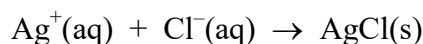
### *Test for specific identification of a halide (T<sub>An2b</sub>)*

If test (T<sub>An2a</sub>) is positive, the identity of the halide is distinguished by oxidation of the halide ion (X<sup>-</sup>) to free halogen (X<sub>2</sub>), which is easily recognised by its colour. To accomplish this, the solid unknown is oxidised with manganese dioxide in the presence of sulfuric acid.



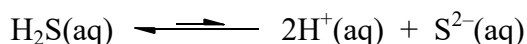
### *Test for Ag<sup>+</sup> and Pb<sup>2+</sup> (T<sub>Cut1</sub>)*

The solid is dissolved in nitric acid and hydrochloric acid added. The presence of a white precipitate indicates the presence of Pb<sup>2+</sup> or Ag<sup>+</sup>.

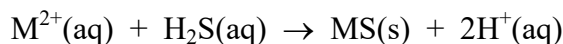


***Test for Cd<sup>2+</sup>, Cu<sup>2+</sup> and Sn<sup>2+</sup> (T<sub>Cat2</sub>)***

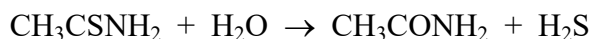
The concentration of S<sup>2-</sup> ions in a solution of H<sub>2</sub>S can be reduced to extremely low levels by making the solution acidic. The following equilibrium lies very much to the left.



The high concentration of H<sup>+</sup> ions forces the equilibrium to move even further to the left. Under these conditions of extremely low S<sup>2-</sup> concentration, only the most insoluble metal sulfides (*i.e.* CdS, CuS and SnS) will precipitate.



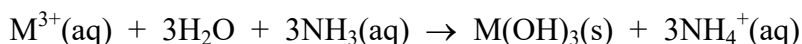
The aqueous H<sub>2</sub>S is generated *in situ* from thioacetamide, which is hydrolysed under the acidic conditions.

***Test for Fe<sup>3+</sup>, Cr<sup>3+</sup> and Al<sup>3+</sup> (T<sub>Cat3</sub>)***

These cations have the most insoluble hydroxides. The concentration of OH<sup>-</sup> must be very low in order to avoid precipitating hydroxides of other cations. An NH<sub>4</sub>Cl/NH<sub>3</sub> buffer solution is used to achieve the necessary conditions. Ammonia, NH<sub>3</sub>, is a weak base that hydrolyses only slightly. In the presence of ammonium ion, NH<sub>4</sub><sup>+</sup>, this hydrolysis is even more suppressed, and the resultant [OH<sup>-</sup>] is in the order of 10<sup>-5</sup> M.



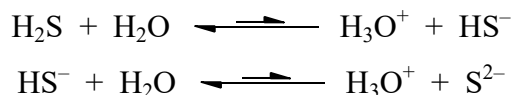
The sample is dissolved in nitric acid and heated for several minutes. This not only dissolves the solid, but also oxidises any Fe<sup>2+</sup> present to Fe<sup>3+</sup>. A buffer solution of solid NH<sub>4</sub>Cl and 16 M NH<sub>3</sub> is then added. A brown precipitate indicates the presence of Fe<sup>3+</sup> in the solution (although it may have initially been Fe<sup>2+</sup> or Fe<sup>3+</sup> in the solid), a grey or green precipitate indicates Cr<sup>3+</sup> and a white precipitate indicates Al<sup>3+</sup>.



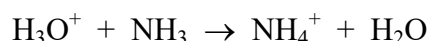


**Test for  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ( $T_{\text{Cat}4}$ )**

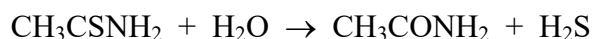
Although all have insoluble sulfides and hydroxides, precipitation of these ions in  $T_{\text{Cat}2}$  and  $T_{\text{Cat}3}$  was avoided because of the very low  $[\text{S}^{2-}]$  and  $[\text{OH}^-]$  respectively. They are precipitated as sulfides in this test under slightly basic conditions because the  $[\text{S}^{2-}]$  is considerably higher.



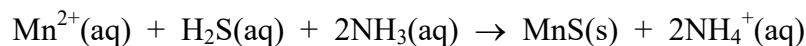
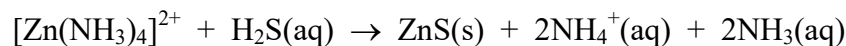
Both these equilibria are pushed to the right in the presence of an  $\text{NH}_4\text{Cl}/\text{NH}_3$  buffer solution. The  $\text{NH}_3$  combines with the  $\text{H}_3\text{O}^+$  ions, creating a greater  $[\text{S}^{2-}]$  than is possible under acidic or neutral conditions.



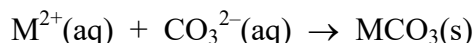
The unknown is dissolved in hydrochloric acid and the buffer of solid  $\text{NH}_4\text{Cl}$  and 16 M  $\text{NH}_3$  is added. The presence of the ammonia converts  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions into their ammine complexes. This was a factor in preventing these ions from precipitating as insoluble hydroxides in test  $T_{\text{Cat}3}$ , as the concentration of free  $\text{M}^{2+}(\text{aq})$  ions in the presence of ammonia is very small. Aqueous  $\text{H}_2\text{S}$  is again generated *in situ* from thioacetamide.



If a precipitate forms, then either  $\text{Ni}^{2+}$  (black from a blue-violet solution),  $\text{Co}^{2+}$  (black from a brown solution),  $\text{Zn}^{2+}$  (white), or  $\text{Mn}^{2+}$  (peach, orange-pink) is present.

**Test for  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Mg}^{2+}$  ( $T_{\text{Cat}5}$ )**

The unknown is dissolved in water or acid and sodium carbonate solution added. A white precipitate indicates the presence of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$ .



To identify the specific cation present, a flame test is performed. No colour (or yellow due to  $\text{Na}^+$  contaminant) indicates  $\text{Mg}^{2+}$ , dull (brick) red indicates  $\text{Ca}^{2+}$ , crimson indicates  $\text{Sr}^{2+}$  and pale green indicates  $\text{Ba}^{2+}$ .