Problem 2 (28% of total)	Question	2.1	2.2	2.3	2.4	2.5	2.6	2.7	Total
	Points	1	2	3	2	1	1	20	30

Problem 2: Onsens, anyone?

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Authors' Note: *It is* ***highly recommended*** *for different members of the team to work on different parts of* ***part 2*** *of this problem at the same time.* ***Part 2*** *has been structured such that individual parts can largely be done independent of each other, except for the ending.*

After learning about the contents of his ordered Onsen bath salts (see silver and gold tier to learn more), Rymh was very curious about *why* there was a white precipitate that formed when he dissolved them in water. Upon further research, he discovered that it was known as 湯の花 (*Yunohana*).

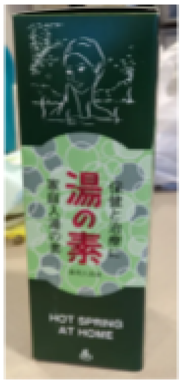

Fig. 3.1: rymh's quirky obsession with onsens

Yunohana refers to the insoluble components[2] of hot springs that precipitate or deposit on their sides. Sometimes, it is collected and sold for use as a bath additive.

Rymh is very curious about how it forms in one particular hot spring, so he does some qualitative analysis to find out.

Part 1: Qualitative Analysis

Rymh took multiple spoonfuls of *Yunohana* and dissolved it completely in water, obtaining solution **FA1** without any solids remaining in the test tube. He then split it into three test tubes. It is known that *Yunohana* contains 2 cations and 1 anion.

To the first test-tube of **FA1**, rymh added $Ba(NO_3)_2$ (aq). A white precipitate was formed.

2.1 Rymh concluded that the anion in **FA1** must be SO_4^{2-}. Orange told him that he is not entirely correct, and there might be other possibilities. **Explain** why rymh is not entirely correct.

2.2 **Suggest** another simple chemical test to confirm that the anion in **FA1** is indeed SO_4^{2-}.

[2] Insolubility is due to concentration, which is why rymh is able to dissolve the *Yunohana* later on in the question.

After confirming that the anion in **FA1** was indeed SO_4^{2-}, rymh moved onto finding the cations.

To the second test-tube of **FA1**, rymh added NaOH (aq). A green precipitate with white streaks which turned into a brown precipitate with white streaks on prolonged standing was observed. Upon addition of excess NaOH and proper shaking, the white streaks disappeared.

To the third test-tube of **FA1**, rymh added NH_3 (aq). He observed the same precipitate as above, with the same observation on prolonged standing. However, upon addition of excess NH_3 and proper shaking, the white streaks remained.

2.3 Based **only** on the two cation tests above, rymh could identify one of the cations, **C1**, but could only narrow down the other cation to two possibilities, **C2** and **C3**. **Identify** **C1**, **C2** and **C3**.

2.4 However, Orange told him that based on the anion test, it was actually possible to narrow down the other cation without doing any other tests. **Identify** and **explain** which cation (between **C2** and **C3**) is actually present in *Yunohana*.

Orange suggested that there was actually a cleaner way to do the qualitative analysis for **FA1** as a confirmatory test. Orange dissolved a new test-tube of *Yunohana* in water, obtaining **FA2**. He then split this into two test-tubes.

Test 1: To the first test-tube, add several drops of $K_3Fe(CN)_6$.
Test 2: To the second test-tube, add several drops of NaCl.

2.5 **State** the observations from performing **test 1**.

2.6 **State** the observations from performing **test 2**.

Part 2: Actual Measurements

Now, rymh is curious about the actual chemical formula for *Yunohana*. He decides to get to the bottom of it by doing some experiments. He dissolves 10.000 g of *Yunohana* into 150 ml of water. He then splits it into three beakers, **FA3** (40 ml), **FA4** (50 ml), **FA5** (60 ml).

To **FA3**, rymh added 250 ml of 0.500 mol dm^{-3} potassium ferricyanide, $K_3[Fe(CN)_6]$, as per **test 1** above and stirred the mixture well. This resulted in a coloured solution, through the ionic equation below. Denoting the cation **C1** as $\mathbf{M}^{x+}$,

$$K^+ + \mathbf{M}^{x+} + [Fe(CN)_6]^{3-} \rightarrow [K\mathbf{M}[Fe(CN)_6]]^{x+}$$

0.100 ml of the coloured solution was then pipetted into a 100 ml volumetric flask using a micropipette and topped up to the top with deionised water. This solution was then transferred into a cuvette and the absorbance measured using a UV-Vis spectrophotometer. The absorbance was 0.4355.

[Molar absorption coefficient, ε = 41760 $dm^3\ mol^{-1}\ cm^{-1}$, path length = 1 cm]

Next, to **FA4**, rymh added 50 ml of 1.000 mol dm^{-3} ethylenediaminetetraacetic acid (EDTA) and heated the mixture with stirring. Denote the correct cation between **C2** and **C3** as $\mathbf{N}^{y+}$.

$$\mathbf{N}^{y+} + EDTA^{4-} \rightarrow [\mathbf{N}(EDTA)]^{(4-y)-}$$

Afterwards, he transferred the solution to a conical flask, and added a few drops of potassium ferrocyanide, $K_4[Fe(CN)_6]$, as an indicator. He then titrated the solution with 1.500 mol dm^{-3} $Zn(NO_3)_2$ until a white precipitate formed at the endpoint. 28.35 ml of $Zn(NO_3)_2$ was needed to reach the endpoint.

$$Zn^{2+} + EDTA^{4-} \rightarrow [Zn(EDTA)]^{2-}$$

$$2Zn^{2+} + [Fe(CN)_6]^{4-} \rightarrow Zn_2[Fe(CN)_6]\ \textbf{(Precipitate)}$$

Next, to **FA5**, rymh added 50 ml of 1.000 mol dm^{-3} $Ba(NO_3)_2$ and stirred thoroughly. He then filtered the mixture. Denoting the anion as $\mathbf{A}^{z-}$,

$$Ba^{2+} + \mathbf{A}^{z-} \rightarrow [Ba\mathbf{A}]^{(z-2)-}$$

To the filtrate, he then added 50 ml of 1.000 mol dm^{-3} K_2CrO_4 and stirred thoroughly. He then filtered the mixture again, and collected the residue. He washed it with deionised water and dried it thoroughly. Using a calibrated weighing boat, he determined that the mass of the residue was 8.112 g.

$$Ba^{2+} + CrO_4^{2-} \rightarrow BaCrO_4$$

Rymh added a small amount of *Yunohana* into a test tube and gently heated it with a bunsen burner. He then holds a piece of dry cobalt chloride paper at its mouth and notices that the blue cobalt chloride paper turns pink.

Then, rymh weighed another 7.000 g of *Yunohana* into a crucible. He heated it until there was no more mass change of the crucible. After subtracting the weight of the crucible, he determined that the final mass of the solid was 3.886 g.

2.7 Determine the empirical formula of *Yunohana*. Show **all** working, as credit will be awarded for partial solutions to this problem.
Do make sure to verify all assumptions made.

Epilogue

Rymh’s curiosity has finally be satisfied. Thank you everyone for joining rymh on his journey (or obsession) with Onsens! We hope you enjoyed the stories as much as we did writing them. 🙂 (See silver and gold tier for the full story)

Problem 3: Solution

3.1) Rymh concluded that the anion in **FA1** must be SO_4^{2-}. Orange told him that he is not entirely correct, and there might be another possibility. **Explain** why rymh is not entirely correct.

> Sulfites (SO_3^{2-}) also give a white precipitate, $BaSO_3$, when $Ba(NO_3)_2$ is added.
> **OR** Carbonates (CO_3^{2-}) also give a white precipitate, $BaCO_3$, when $Ba(NO_3)_2$ is added.
>
> **Grading guidelines**
> 1 point for a correct explanation.

3.2) Suggest another simple chemical test to confirm that the anion in **FA1** is indeed SO_4^{2-}.

> Add a few drops of dilute aqueous HNO_3 to a clean sample of **FA1**.
>
> If there is no **evolution of a colourless, pungent gas (0.5 points)** that **turns aqueous acidified $KMnO_4$ from purple to colourless (0.5 points)**, the anion is indeed SO_4^{2-}.
> **OR** If there is no effervescence of a colourless, odourless gas that forms a white precipitate when bubbled into limewater, the anion is indeed SO_4^{2-}.
>
> **Grading guidelines**
> 1 point for the addition of a dilute acid (preferably HNO_3).
> 1 point for the correct negative observation (important points are marked in green).
> Accept all plausible alternative answers.

3.3) Based **only** on the two cation tests above, rymh could identify one of the cations, **C1**, but could only narrow down the other cation to two possibilities, **C2** and **C3**. Identify **C1**, **C2** and **C3**.

> **C1:** Fe^{2+}
> **C2/C3:** Al^{3+}, Pb^{2+}
>
> **Grading guidelines**
> 1 point for each correct cation identified (Total 3 points).

3.4) However, Orange told him that based on the anion test, it was actually possible to narrow down the other cation without doing any other tests. Identify which cation (between **C2** and **C3**) is actually present in *Yunohana*.

> Al^{3+} is present since Pb^{2+} ions will precipitate with SO_4^{2-} anions.

Grading guidelines
1 point for the correct cation identified.
1 point for correct explanation.

3.5) State the observations from performing **test 1**.

Any of the following will be accepted:

- A deep blue solution is formed.
- A deep blue precipitate is formed.

Grading guidelines
1 point for the correct answer.

3.6) State the observations from performing **test 2**.

No precipitate was formed.

Not accepted: No reaction / Nothing. (Or any statement to that effect)
Reasoning: It is clear that the reason for **test 2** is to distinguish between Al^{3+} and Pb^{2+}. $PbCl_2$ will form a white precipitate, so the negative observation is that **no precipitate** is formed.

Grading guidelines
1 point for the correct answer.

3.7) Determine the empirical formula of *Yunohana*. Show **all** working, as credit will be awarded for partial solutions to this problem.

Do make sure to verify all assumptions made.

Empirical Formula: $FeAl_2(SO_4)_4 \cdot 22H_2O$.

Grading guidelines

For the verification of assumptions, any **1 point** made will be accepted.

Determination of Fe^{2+} (4 points working + **1 point assumption**)

- 1 point for calculating the concentration of Prussian blue using Beer-Lambert's Law.
- 1 point for calculating the concentration of Prussian blue before dilution.
- 1 point for calculating the number of moles of Fe^{2+}.
- 1 point for adjusting it to the original amount of *Yunohana* before the solution was split.
- **1 point for verifying that potassium ferricyanide is in excess by calculating the number of moles of potassium ferricyanide.**
- **1 point for verifying that Beer-Lambert linearity holds because the absorbance is between 0.2 to 0.5.**

Determination of Al^{3+} (4 points working)

- 1 point for calculating the number of moles of Zn^{2+} titrated.
- 1 point for calculating the number of moles of EDTA originally present.
- 1 point for calculating the number of moles of EDTA used and therefore the number of moles of Al^{3+} present.
- 1 point for adjusting it to the original amount of *Yunohana* before the solution was split.

Determination of SO_4^{2-} (5 points working + **1 point assumption**)

- 1 point for calculating the molar mass of $BaCrO_4$.
- 1 point for calculating the number of moles of $BaCrO_4$.
- 1 point for calculating the number of moles of $Ba(NO_3)_2$ added.
- 1 point for calculating the number of moles of $Ba(NO_3)_2$ used and therefore the number of moles of SO_4^{2-} present.
- 1 point for adjusting it to the original amount of *Yunohana* before the solution was split.
- **1 point for verifying that potassium chromate is in excess by calculating the number of moles of potassium chromate.**

Determination of H_2O (3 points working)

- 1 point for calculating the difference in the mass of solid before and after heating, **and identifying that the difference is due to water** based on the cobalt chloride paper test.
- 1 point for calculating the number of moles of water.

- 1 point for adjusting it to the original amount of *Yunohana* before the solution was split.

Overall (1 point working + 1 point answer)

- 1 point for calculating the mole ratio of the different components of *Yunohana*
- 1 point for the correct empirical formula.