

Problem 3 (25% of total)	Question	3.1	3.2	3.3	3.4	3.5	3.6	3.7	3.8	Total
	Points	1	7	12	3	1	1	4	8	48
		3.9	3.10	3.11						
		6	4	1						

Problem 3: Onsens, anyone?

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

Rymh received an unknown package in his mail. Despite the risk of getting Anthrax from frustrated ACOT participants, he believed that it was the Japanese onsen concentrate, *Yunomoto*, that he ordered from a Yahoo! auction on Buyee. So he rips the package open — fortunately, there's no Anthrax in there.

When preparing the bath for the first time, rymh accidentally spilled a few drops onto his fingers. The concentrate turned out to be pretty corrosive, as rymh found out the hard way (it stung his fingers).

Curious, rymh decided to search up the ingredients list to figure out the ingredient responsible for the concentrate's corrosive properties. However, a quick google search in Japanese brings up only two active ingredients in the product:

■有効成分
多硫化態硫黄・酸化カルシウム

■ Active ingredients
Polysulfide sulfur/calcium oxide

*Powered by Google Translate.

Rymh figures that the mixture cannot just be made from these two ingredients alone, and decides to conduct some tests on it to ascertain the identity of other ingredients in there. Of course, "polysulfide sulfur" also sounds very suspicious, so he decides to determine the *actual* sulfur-containing compounds present in the concentrate.



Fig. 3.1: rymh's quirky obsession with onsens

Introduction: Strange Smells and White Powder

Before even beginning proper tests to figure out the identity (or identities) of any compounds present, he first decided to enjoy a good, long, soak in the bathtub. Of course, he added a capful of *Yunomoto* to the bathtub, as per the directions stated on the packaging. There was a faint but familiarly unpleasant smell, but he paid it no mind and went ahead. *After all, since it's one of the highest-rated bath additives in Japan, it's probably still safe to use, right?*

When the concentrate was added to the tub, it formed a slightly murky yellowish-green solution. Interestingly, Rymh noted that the yellowish-green colour faded, and a white precipitate formed over time.

3.1 What is the identity of the compound most likely responsible for the 'faint but familiarly unpleasant smell'?

H₂S. [1]

Before stepping into the bath, Rymh decided to scoop a sufficiently large sample of the now-white and murky solution. He poured the mixture over a large coffee filter, and left it alone while he enjoyed the nice bath.

After finishing his bath, he came back to the filtration setup and discovered that the mixture separated into a colourless filtrate and a white residue. He washed the white residue with deionized water and left it to dry for a full day.

Part 1: What's the Solution?

While waiting for the white residue to dry, he decided to analyze the contents of the solution. For the first test, he added 0.10 ml of 0.010 M K₂CrO₄ solution to a 20.00 ml aliquot of the filtrate. He then proceeded to titrate it with a solution of 0.20 g of AgNO₃ in 1000 ml of water. When he added the first drop, he noticed that a white precipitate was forming. He thought it was a great sign and continued adding more AgNO₃ solution. After adding 54 ml of the AgNO₃ solution, the precipitate finally turned orange.

3.2 What ion did Rymh try to analyze? What is the concentration of this ion? Give Rymh three pieces of advice on how to improve the accuracy of his procedure.

This procedure is for the determination of Cl⁻ ions. (1 pt)

Usually, the titration is ended when the orange precipitate of Ag₂CrO₄ appears and the added volume is directly used to calculate the concentration of chloride in the sample. However, both the sample and the AgNO₃ solution are very dilute so this approach would

lead to a gross overestimation (bonus **1 pt** if you did that). Instead, we have to use the solubility product of Ag_2CrO_4 to calculate the concentration of Ag^+ at the apparent endpoint and find the “real” endpoint.

$$K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) = 2.048 \times 10^{-12} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \Rightarrow [\text{Ag}^+] = (K_{\text{sp}}/[\text{CrO}_4^{2-}])^{0.5}$$

$$[\text{CrO}_4^{2-}] = 0.010 \text{ M} \times 0.10 \text{ ml} / (20 + 0.1 + 54) \text{ ml} = 1.350 \times 10^{-5} \text{ M}$$

$$[\text{Ag}^+] = (2.048 \times 10^{-12} / 1.350 \times 10^{-5})^{0.5} = 3.895 \times 10^{-4} \text{ M}$$

The amount of Ag^+ ions in the solution at the apparent end point is therefore

$$n(\text{Ag}^+) = 3.895 \times 10^{-4} \text{ M} \times (0.054 + 0.020) \text{ L} = 2.882 \times 10^{-5} \text{ mol}$$

$$\text{The concentration of the titrant is: } 0.2 \text{ g} / (169.87 \text{ g/mol} \times 1 \text{ L}) = 1.177 \times 10^{-3} \text{ M}$$

The volume added *after* the real endpoint is therefore:

$$2.882 \times 10^{-5} \text{ mol} / 1.177 \times 10^{-3} \text{ M} = 0.0245 \text{ L} = 24.5 \text{ ml}$$

The real endpoint was achieved at $54 - 24.5 = 29.5 \text{ ml}$ of titrant

$$n(\text{Cl}^-) = n(\text{Ag}^+) = 29.5 \text{ ml} \times 1.177 \times 10^{-3} \text{ mmol/ml} = 34.7 \times 10^{-3} \text{ mmol}$$

$$[\text{Cl}^-] = 34.7 \times 10^{-3} \text{ mmol} / 20 \text{ ml} = 1.74 \times 10^{-3} \text{ M} \text{ (3 pt)}$$

Rymh could do much better! He could have repeated the titration multiple times for better accuracy, used more accurate equipment to measure masses and volumes (the answer should have just 2 significant figures, though I won't penalise for that), or used additional tests to see if there are any ions that interfere with the procedure (such as carbonate or phosphate). **(3 pts)**

Part 2: Elucidation Fun

By the following day, the white residue had dried into a white powder. Knowing that Ca^{2+} was present in the sample, he decided to separate it out before performing further tests, which he thankfully managed to do (with the help of some black magic).

Upon strong heating, the white powder turned black, and there was a notable loss in mass. To determine the identity of the ions present in the sample, he then performed a series of tests as shown on the next page. In the scheme, the red boxes refer to tests conducted that give no positive results. They are always done **before** the tests that yielded positive results are conducted.

Black powder

1. 6 M NH_4OH
2. 6 M HCl , excess
3. H_2S

6 M HCl dropwise

colourless filtrate

Black ppt

toluene

Black ppt

Yellow filtrate

$(\text{NH}_4)_2\text{S}_x$, filter

colourless filtrate

1. 3 M H_2SO_4
2. Evaporate until SO_3 fumes
3. cold H_2O

no ppt observed

NH_4OH until pH > 7

Deep blue filtrate

White ppt

excess HNO_3

Colourless filtrate

1. NH_4OH until pH > 7
2. Na_2SnO_2

Black ppt

White ppt

Green filtrate

1. 6 M NH_4OH , excess
2. H_2S

Black ppt

Colourless filtrate

evaporation to dryness

No remaining residue

no ppt observed

excess 1 M HCl

1. Heat
2. 2 eq. 6 M HNO_3 , heat
3. 10 eq. 6 M NH_4OH
4. 5 eq. $(\text{NH}_4)_2\text{CO}_3$

??? ppt

1. excess 6 M NaOH , H_2O
2. Na_2O_2 slowly
3. Heat

??? ppt

1. excess 16 M HNO_3
2. 1 g KClO_3
3. Heat carefully

Black ppt

Orange filtrate

white ppt

1. Hot 6 M HNO_3 , cat. H_2O_2 (ppt dissolves)
2. $\text{NaBiO}_3(\text{s})$

Violet solution

NH_4OH until pH > 7

Brown ppt

red ppt

1. 5 cm³ 1 M HCl
2. 5 cm³ 3 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$
3. 5 cm³ compound A
4. 4 cm³ 6 M NH_4OH + 1 cm³ 3 M $(\text{NH}_4)_2\text{CO}_3$

He determined that the heated black powder consisted of a relatively inert macromolecule and 5 other cations of different elements.

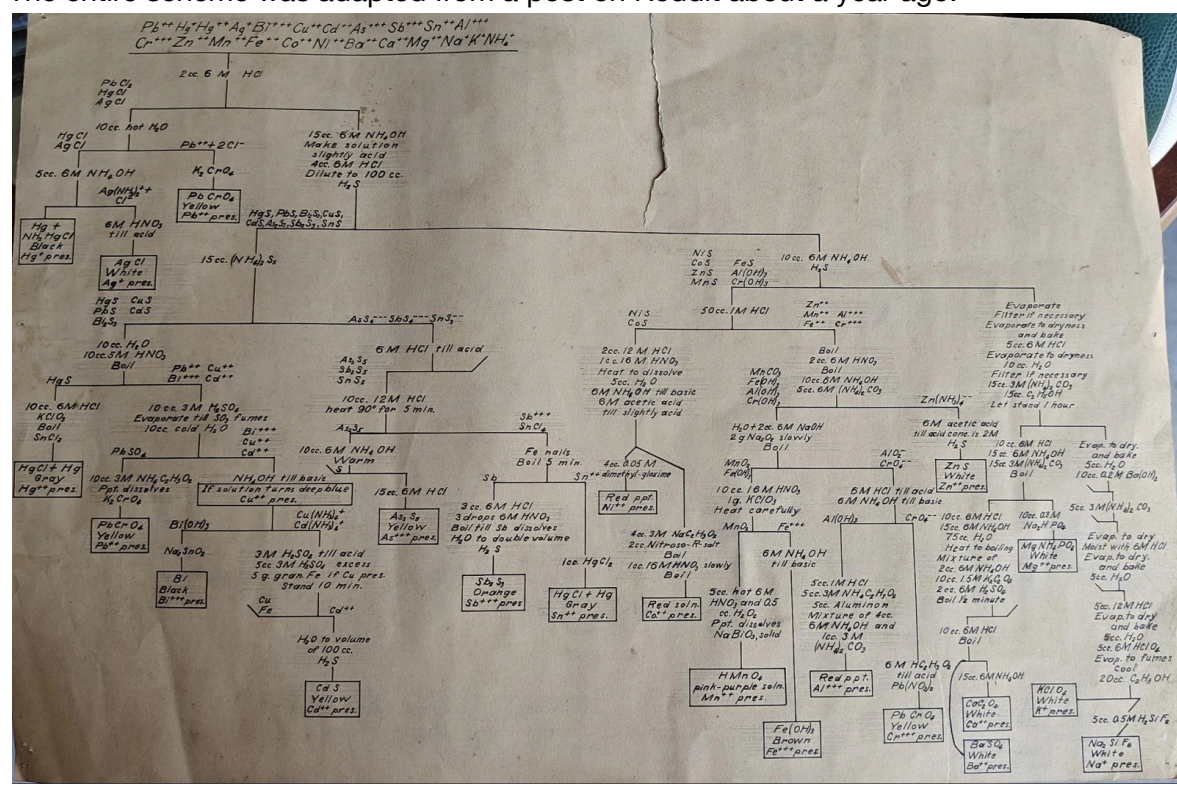
3.3 **Determine** the identities of the 5 cations present in the black solid, explaining your reasoning clearly. **What** is the most likely identity of the macromolecule present?

[Hint: Don't overthink about why the pre-heated powder is white.]

- [1] for determining the absence of Pb^{2+} , Hg^{+} or Ag^{+} (stating just one will suffice).
 [1] for determining the absence of As^{3+} , Sb^{3+} or Sn^{2+} (stating just one will suffice).
 [1] for determining presence of Cu^{2+} .
 [2] for determining the presence of Bi^{3+} .
 [1] for determining the absence of Ba^{2+} , Zn^{2+} or Mg^{2+} (stating just one will suffice).
 [2] for determining the presence of Fe^{3+} .
 [1] for determining the presence of Al^{3+} .
 [2] for determining the presence of Mn^{2+} .
 [1] for stating that the macromolecule present is likely SiO_2 .

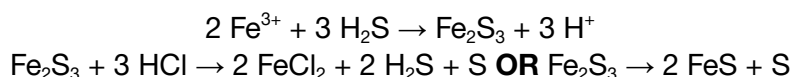
Note:

The entire scheme was adapted from a post on Reddit about a year ago:



3.4 State a possible reason for the presence of the yellow filtrate in the scheme, and cite a piece of evidence from the scheme to support your reasoning. Write down relevant equation(s) responsible for its formation.

The yellow filtrate is dissolved elemental sulfur:



Fe^{3+} reacts with the bubbled H_2S to form Fe_2S_3 , which decomposes at room temperature to give FeS and elemental sulfur. **OR** Fe^{3+} reacts with the bubbled H_2S to form Fe_2S_3 , which decomposes with the excess HCl to give FeCl_2 , H_2S and elemental sulfur.

This is further evidenced by the fact that the filtrate is green, which is characteristic of Fe^{2+} (note: FeS is soluble in acids).

[1] for identifying that the yellow filtrate is elemental sulfur.

[1] for either decomposition reaction given (both are likely to occur).

[1] for stating the correct supporting evidence.

3.5 State the identity of compound **A** in the scheme.

Aluminon. **[1]**

To make sure of the identity of the inert macromolecule, he decided to perform IR analysis on a suspension of an isolated sample of it in mineral oil.

3.6 Other than peaks caused by the solvent (or any interactions the solvent may have with the sample), **state** the number of peaks that he should expect to see in the FTIR spectrum of the sample. Assume that the peaks caused by the presence of the solvent do not overlap with the peaks caused by the macromolecule sample.

2 peaks.

[1] for correct answer stated.

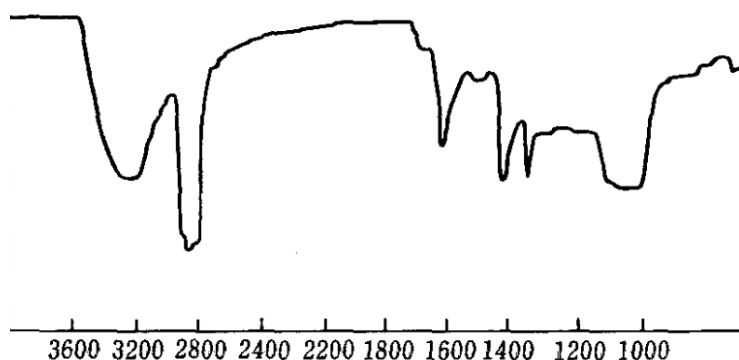
Part 3: Abroad in Korea?

After some time, Rymh realized that he was never really going to be satisfied with mere bath additives. He wanted the real thing — so he went on a trip to Korea to enjoy some natural hot springs.

In one of the hot springs that he visited in Korea, he found signs noting the presence of a particular species of thermophilic bacterium in the hot spring water. Mildly interested, he collected a sample of water from the hot spring and brought it back home.

Back home, he isolated the bacterium and left it to reproduce at optimal conditions (~70

°C). Then, he extracted the lipids from the cells and analyzed the resulting sample using FTIR spectroscopy as shown below.



“Don’t bother trying to find this diagram online.”

Upon analyzing this FTIR spectrum, Rymh realized that one unique characteristic about the bacterium’s membrane structure.

3.7 Describe the unique characteristic Rymh observed and **discuss** its likely significance in context of the bacterium habitat’s extreme conditions.

Rather than the expected peak at 1735–1740 cm^{-1} indicating the presence of ester bonds in the membrane lipid, there is a peak at 1100 cm^{-1} indicating the presence of ether bonds instead.

This suggests that the lipid constituents contained exclusively ether linkages without any long-chain fatty acid derivatives present. Hence, this suggests that the replacement of ester-linked lipids by ether linkages may be advantageous in stabilizing membrane structures for living organisms living in extremely high temperature environments.

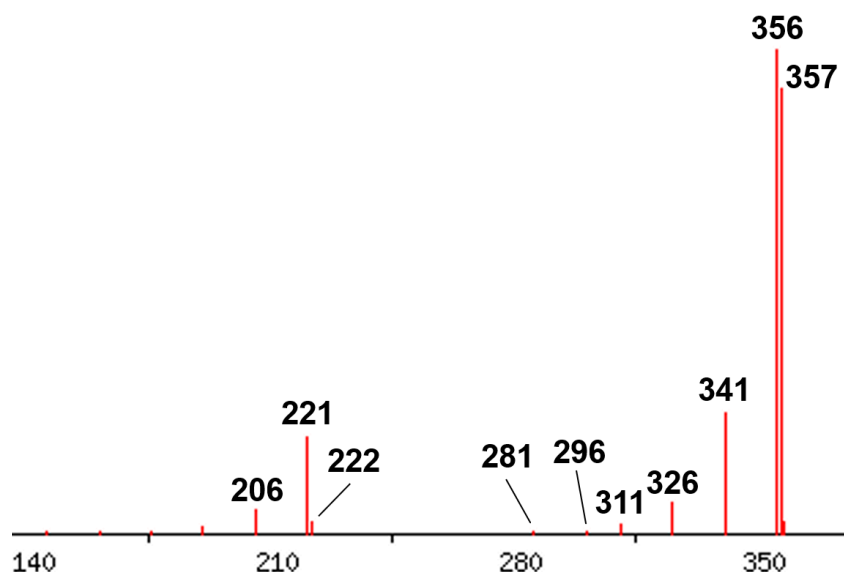
<https://www.tandfonline.com/doi/epdf/10.1080/00021369.1977.10862747?needAccess=true>

[2] for noting the presence of ether bonds instead of the ester bonds expected.

[2] for discussing its significance with relation to the bacterium’s habitat.

Another hot spring he visited contained two specific isotopes of a particular element **X**. As a mad synthesis fan, he couldn’t resist bringing a large sample of this hot spring water back home too.

In a research lab back home, he isolated pure element **X**, and carried out a series of reactions to synthesize ternary compound **Y**. The mass spectrum of compound **Y** is shown below, with only selected peaks shown.



"It's a simulated spectrum — dont even bother trying to find this online."

Notably, the ratio of the peaks at $m/e = 221$ and $m/e = 222$ is roughly 9 : 1. There also exists an additional peak at $m/e = 342$ that is not shown on the spectrum. The intensity of the $m/e = 342$ peak is lower than that of the $m/e = 341$ peak.

3.8 Identify element **X** and compound **Y**, clearly explaining your reasoning. Which city did Rymh visit? Which two isotopes of element **X** are present in the hot spring water?

Element **X**: Sr (isotopes: ^{86}Sr and ^{87}Sr)

Compound **Y**: $\text{Sr}(\text{Cp-Me}_5)_2$

City: Busan

[1] for determining the presence of two identical ligands of mass 135 each.

[1] for stating presence of 5 Me groups on each ligand.

[2] for deducing the presence of Cp-Me₅ ligand.

[1] for deducing identity of compound X.

[1] for stating the identity of compound Y.

[1] for stating the city visited by Rymh.

[1] for stating the two isotopes of element X present in the hot spring water.

Mass spec input data:

358 2.2

357 92

356 100

341 25

326 6.25

311 1.5625

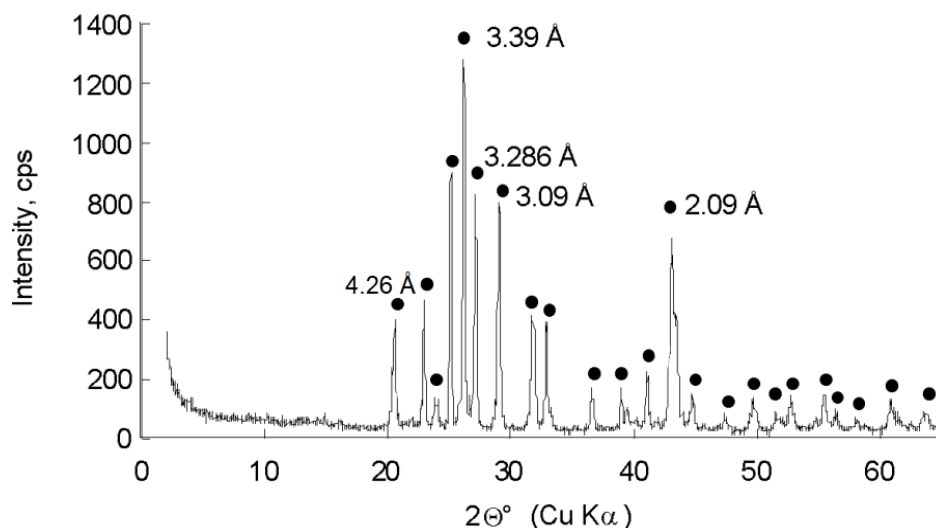
301 0.390625

286 0.09765625

222 2.2
 221 20
 206 5
 191 1.25
 176 0.3125
 161 0.078125
 146 0.01953125

Part 4: Radioactive spring

Rymh is still heavily obsessed with hot springs, and once he heard about the existence of radioactive hot springs on Earth, he couldn't help but visit them immediately. During his second trip, he illegally collected some minerals around the hot spring. First, Rymh takes powder X-ray diffraction (XRD). It is known that this mineral consists of 2 simple salts with common anion, and both are insoluble in water. Both cations are on the same period and have same oxidation state.



3.9 Determine the composition of this mineral with the help of an online database. Also, **write** down which peaks you used to determine the composition of the mineral.

PbSO₄ and BaSO₄, hokutolite is (Ba,Pb)SO₄

One can use this database to find possible minerals

<https://webmineral.com/help/XRayDiffraction.shtml>

For barite,

<https://webmineral.com/MySQL/xray.php?lambda=1.54056+-+CuKa1&lambda1=&ed1=3.39&ed2=3.09&ed3=2.09&minmax=10&chem=&submit=Submit>

3.396(26.22)	100	2.848(31.38)	31	2.078(43.52)	29	Pertlikite	K ₂ (Fe ⁺⁺ Mg ₂ (Mg ^{Fe++}) ₄ Fe ⁺⁺ 2Al(SO ₄) ₂ ·18H ₂ O
3.400(26.19)	100	3.380(26.35)	100	2.000(45.30)	100	Ardaite	Pb ₁₉ Sb ₁₃ Sn ₃ Cl ₇
3.420(26.03)	100	3.370(26.43)	65	2.200(49.99)	60	Sillimanite	Al ₂ SiO ₅ = Al ₂ (SiO ₃) ₂
3.442(25.86)	100	3.101(28.77)	97	2.120(42.61)	80	Barite	BaSO ₄
3.470(25.65)	100	3.090(28.87)	100	2.050(44.14)	100	Sulfoborite	Mg ₃ B ₂ (SO ₄)(OH) ₈ (OH) ₂ F ₂
3.472(25.64)	100	2.956(30.21)	54	2.052(44.10)	46	Scanite	Pb ₁₄ Sb ₃₀ Sn ₅ As ₅ O ₅
3.490(25.50)	100	3.220(27.68)	80	1.989(45.57)	60	Treasureite	Ag ₇ Pb ₆ Bi ₁₁ SS ₃₂

For anglesite, this one is tricky because the concentration of Pb is lower than Ba, so the intensity is not in decreasing order.

<https://webmineral.com/MySQL/xray.php?lambda=1.54056+-+CuKa1&lambda1=&ed1=3.09&ed2=4.26&ed3=3.286&minmax=10&chem=&submit=Submit>

2.920(30.59)	100	4.380(20.26)	90	3.440(25.88)	55	Tinacronite	Na ₆ (BaO ₅ (OH) ₄) ₂ ·4H ₂ O
2.925(30.54)	100	4.640(19.11)	100	3.151(28.30)	100	Amblygonite	(Li,Na)Al ₃ (PO ₄) ₂ (F,OH)
2.943(30.35)	100	4.480(19.80)	90	3.445(25.84)	90	Stillwellite-(Ca)	(Ca,La,Ca)BSiO ₅
2.960(30.17)	100	3.940(22.55)	100	3.050(29.26)	100	Cataclite	(Na,Ca)[₁₂ Si ₃ O ₉ -2(H ₂ O)]
2.960(30.17)	100	3.960(22.43)	80	3.060(29.16)	80	Calcicocataclite	(Ca)[₁₂ Si ₃ O ₉ -2(H ₂ O)]
3.001(29.75)	100	4.260(20.83)	87	3.333(26.72)	86	Anglesite	PbSO ₄
3.024(29.51)	100	4.420(20.07)	91	3.493(25.48)	88	Ximengite	BiPO ₄
3.040(29.36)	100	4.290(20.69)	90	3.170(28.13)	80	Cometite	Cu ₃ (PO ₄)(OH) ₃
3.050(29.26)	100	4.000(22.21)	100	3.406(26.14)	100	Calcicouranite	(Ca,Ba,Pb) ₂ (OH) ₂ (H ₂ O)
3.052(29.24)	100	4.195(21.16)	100	3.070(29.06)	100	Anthoinite	AlWO ₃ (OH) ₃

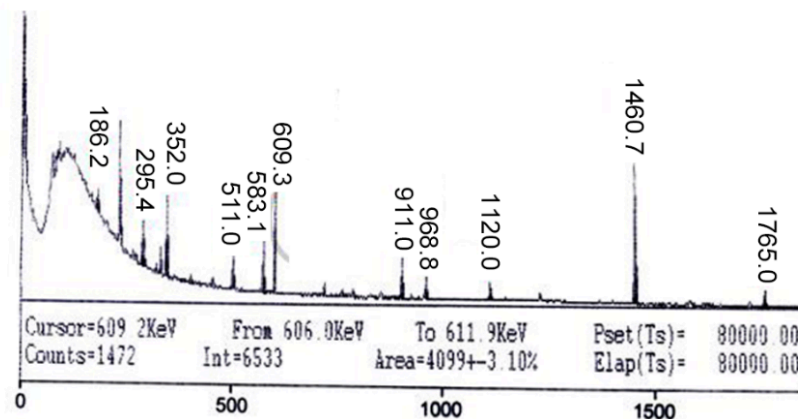
[1.5] for BaSO₄, barite, [1.5] for peaks (3.39, 3.09, 2.09)

<https://webmineral.com/data/Barite.shtml>

[1.5] for PbSO₄, anglesite, [1.5] for peaks (3.09, 4.26, 3.286)

<https://webmineral.com/data/Anglesite.shtml>

Also, during the trip, on a moonless night, he sneaks into the source of the hot spring and takes a gamma-ray spectroscopy of the hot spring source itself. The GRS spectrum is provided below.



3.10 Assign the peaks in the GRS spectrum and **identify** the parent nuclides in the hot spring.

186.2 Ra226
 295.4 Pb214
 352.0 Pb214
 511.0 Ti208
 583.1 Ti208
 609.3 Bi214
 911.0 Ac228
 968.8 Ac228
 1120.0 Bi214
 1460.7 K40

1765.0 Bi214

Parent nuclides: Ra226, Th232 and K40

For spectra of Ra226, thorium and K40, see

<https://gammadb.nuclearphoenix.xyz/overview/>

[2] 0.4 for each peak, max 2pts.

[0.5] for K40, [0.5] for Ra226 or U238, [1] for Th232

3.11 Where in the world could Rymh have visited?

Tamagawa Hot Spring in Akita Prefecture, Japan, **OR** Beitou Hot Spring in Taipei City, Taiwan. Either one is accepted. **[1]**

<https://en.wikipedia.org/wiki/Hokutolite>

Epilogue

After this adventure, rymh was slightly addicted to Onsen bath salts. He then aspires to investigate the white precipitate known as 湯の花 (Yunohana), typically found in Onsens, in more detail. To continue with his adventures, see Bronze Tier, Team Round, Problem 3! For a **slightly** nerfed version of this question, see Silver Tier, Team Round, Problem 3!