Aug, 13, 2014

MEMORANDUM TO: Dr. Mojmir Nemec

FROM: Hyuncheol Kim, KAERI, and Republic of Korea

Subject: Submission of a revised manuscript

Dear Dr. Nemec,

      My co-authors and I appreciate the constructive reviews by Dr. Nemec and Dr. Geist. We now feel that the revised manuscript adequately addresses most of the concerns identified.

Sincerely,

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Response to referee #1

We appreciate the constructive comments of referee #1, and in the revised manuscript have addressed the issues raised. The major issues and our responses are summarized below.

1. **The paper is relatively long (26000 characters) exceeding the allowed 20000. There are repeating parts and pieces of procedures, which could be removed or written united at one place:** The manuscript is revised with 21000 characters. Some references were removed to shorten manuscript. The revised contents were written in blue color.

2. **The scheme of the procedure (Fig.4) is clear and contains all the information. But its description in the text does not and it is hardly to read and understand. Please rewrite the respective parts, the quality of the paper will really increase:** We revised the description of the procedure in 'recommend procedures' section.

3. **You are presenting here the advantage of the automatic system, but disconnection and re-connection of TEVA and Sr-resin columns is done manually. Why? Is it just because of testing of such system rebuild/connection? There is no discussion, why this connection is better than simple peristaltic pump and manual 3-way valves between the columns:** MARS was originally designed for automated separation for single radionuclide of the four samples. This study expands the applicability of our MARS for sequential separation even including minimal manual work, such as disconnection/reconnection of columns. As described in the manuscript (line 74-84), all chemical separation on this system were controlled through the user friendly software developed in our laboratory. It does not need the replacements of chemical composition for washing/elution solution. This study is the middle phase to develop the fully automated system for sequential separation for two radionuclides.

4. **It seems that there are some parameters, which were not tested or the testing was not presented and discussed (e.g. influence of Ca, Mg, Sr concentrations, used flow rates and its dependence, yields of co-precipitation of Pu and Pu(III) oxidation/reduction) which could be crucial for the procedure (yield, MDA…) . Why? Could you correct/discuss this?:** We added the flow rates at every chemical separation step (line 106-146). The effect of Ca on Sr recovery was discussed (line 159-162). As mentioned in 'Result and Discussion' section, high level of Ca in sample before introducing purification step results in small deterioration of Sr recovery on Sr resin. We didn't check that all Pu was oxidized to Pu (III) with co-precipitation of $Fe(OH)_2$. In addition, oxidation state of Pu (IV) before loading on TEVA resin was checked. We expect that the valence adjustment of Pu in concentration step works well. We discussed that the incomplete valence adjustments of Pu may cause the deterioration of Pu recovery.

5. **Too long and complicated sentences are very often used in the text:** See our response to major comment #1.

6. **Table 2 was corrected and revised:**

The concept of 'relative error' was replaced by 'difference' as follows:
Difference = (measured value – known value) / known value x 100.

The concept of difference is generally understood by people. Therefore, we did not define "difference" to shorten the manuscript.

We found the big mistake in table 2. The relative error ('difference', now) for Sr and Pu was wrongly calculated in the original manuscript. It was re-calculated in table 2 (blue colored). In addition, Pu recovery for 10 L seawater was previously stated 85.0 % and 73.3 %. They were wrong values. In the original manuscript, the average value of Pu recovery for five 1 L and two 10 L seawater samples was stated with *62.5 %* (line 198). When Pu recovery for two 10 L seawater is *56.5 %* and *51.8 %*, the average value for Pu recovery is 62.5 %. We changed "*85.0 %, 73.3 %*" to "*56.5 %, 51.8 %*" (blue colored).

Other minor editorial comments:

1. comment (A2): We have replaced "column volume, CV" with "bed volume, BV".

2. comment (A3): It was revised in line 14-15.

3. comment (A4): We added $Na_2S_2O_5$ as a reducing agent.

4. comment (A6): We added the information of particle size of TEVA and Sr resin in line 31.

5. comment (A7): The concentration of strontium in seawater (salinity 3.5 %) was generally known as 8 ppm. In this study, the concentration of strontium was 6.5 ppm. We decided to delete this statement to shorten the manuscript.

6. comment (A8): We revised it in line 78-83.

7. comment (A9): We have monitored the target radionuclide – strontium and plutonium – during elution step (Fig 2-b, Fig 3). The part of the initial eluent volume was collected into 50 ml tube through the left outlet port of 3W-FDV. We can collect the target radionuclides as much as possible, therefore.

8. comment (A10): The statement (pH 2) in the original manuscript is right. We revised the Figure 4. In addition, the volume of 8 M HNO_3 for washing Sr resin has changed "30 ml" to "20 ml" (Fig 4-a). We stated that 20 ml of 8 M HNO_3 was used to wash Sr resin column in the original manuscript (line 190).

9. comment (A11): We did not test the yield of plutonium with various pH. We thought that pH 2 was the reasonable condition for the analysis of actinides in aqueous samples. However, we will check it in the future.

10. comment (A12): see response to comment (A4).

11. comment (A13): We revised it in line 90-94.

12. comment (A14): We added Fe^{3+} as $FeCl_3 \cdot 6H_2O$.

13. comment (A15): We adjusted pH with 25 % ammonia. It was stated in revised manuscript (line 92).

14. comment (A16): The yellow part was revised in line 90-95.

15. comment (A17): We informed the flow rates on every step in revised manuscript.

16. comment (A18): We agree with this referee's comment. See our response to major comment #4.

17. comment (A19): In the concentration step, most of Ca and Mg was precipitated with Sr. The chemical yield of Sr on Sr resin was quantitative up to 320 mg Ca per Sr resin 2 ml (BV) (*Eichrom Technologies*). In this study, we used two times of Sr resin (4 ml BV) for 350 mg Ca in our seawater samples. We thought that the effect of Ca on the recovery of Sr was negligible. As stated in Result and Discussion section, the lower recovery of Sr in 10 L seawater may be attributed to calcium in sample.

18. comment (A20): We added the information of volume in line 123.

19. comment (A22): We added the process of electrodeposition in line 43-45.

20. comment (A23): We changed "NH_3" to "ammonia".

21. comment (A24): See our response to major comment #3.

22. comment (A28): We revised it line 110-112.

23. comment (A30): We added the definition of "DIW" in line 33.

24. comment (A31-34): We revised it in line 129-142.

25. comment (A35): We used the standard solution to test just the purification step (line 120-126).

26. comment (A36); We revised it in line 165-166.

Response to referee #2

We appreciate the constructive comments of referee #2. Our responses to referee 2's comments and suggestions, which have been incorporated in the revised manuscript, are as follows:

1. The sequential separation of Pu and Radiostontium from seawater after nuclear accident can be considered only if radioactive isotopes ^{89}Sr and ^{90}Sr are included in the method. Please revise and explain why ^{89}Sr is not considered. Discuss complications coming up during Cherenkov radiation detection (line 132): We agreed with this referee. The level of ^{89}Sr in seawater is higher than ^{90}Sr in early phase of emergency situation. However, we could not analyze ^{89}Sr because we unfortunately did not have it at that time. We thought that it is not appropriate that we say this in the manuscript. We discussed the analysis of ^{89}Sr by Cerenkov counting in line 173-175 – "In emergency situation, ^{89}Sr level is high, also. The analysis of ^{89}Sr was not shown in this work. However, if $^{89/90}$Sr results are required, Cerenkov counting is useful technique for determination of $^{89/90}$Sr"

2. Carefully revise the format of the text (eg. Indexes-line 51): We revised and shorten the manuscript.

3. Description of precipitation/coprecipitation is hardly to understand. Please specify chemicals used in the procedure. (line 98-104): We revised the concentration step in line 90-104.

4. Please show concentrations of mentioned interfering elements. (eg. line106): See our response to major comment #4 of referee #1.

5. Have you checked that all Pu is reduced? (line 102): See our response to major comment #4 of referee #1.

6. The description of the recommended procedure is unclear and reader is not sure what is washing solution, working solution etc., what is the sequence of the steps. Please clarify it and be consistent with Fig.4. (line 177 – 194): The recommended procedure was described in Results and Discussion section (line 133-146).

7. References are not in JRNC form: In references section, the name of all authors was shown.

8. Please explain indexes in Table 1: We revised it.

9. Table 2 was corrected and revised: We found mistakes in table 2. See our major response #6 to referee #1.

Other minor revision:

We changed "Biochem Fluidics, USA" to "Benchmark, Omnifit, USA" in line 58.