The Analysis of Tritium in Natural Water

do Electrolysis Enrichment using Solid Polymer Electrolyte

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ABSTRACT

Solid Polymer Electrolyte (SPE) is a cation exchange resin, and applied to tritium enrichment by electrolysis technique to have functioning as an ionic conduction. The experiments were carried out using the latest model, SPE-1000 prototype, which developed from previous model, SPE-500. The results were found that the cooling units of SPE-1000 prototype are not efficient to cool down and condense the vapour. A high current, 50 amper applied to electrolytic system made the system hot and temperature rose up to 50 degree celsius.

For test run, initial volume 1000 ml. was electrolysed for 2.3 days until reaching the final volume 75 ml. that fixed at each run by using level sensor. Five runs using tritium spiked samples shown the reproducibility was a little poor, the variation of the concentration factor (Tf/Ti) was 8.3 ± 0.40 and the relative standard deviation was 4.8%. The apparent sepearation factor was calculated to be 5.78. The experiments established a linear relationship between concentration factor (Tf/Ti) and its initial volume (Vi) providing an equation of tritium content in sample as

\[ Ti = Tf \cdot 10^{(0.827 \log(Vi) - 1.587)} \]

As the electrolytic system was found memory effect which keep the the tritium activity from previous run. We should carry out the procedures as follow. 1) wash by using 400 ml. of deionized water and apply current at 50 ampere for 10 minute twice. When the above procedures were done then 2) wash by 400 ml. of tritium-free water 50 ampere apply for 10 minutes twice, the decontamination factor was approximately 1000.
1. OBJECTIVE

1.1 To examine the performance of the SPE-1000 prototype
1.2 To determine the relationship between concentration factor and initial volume

2. INTRODUCTION

Solid Polymer Electrolyte (SPE) is a kind of cation exchange resin which sulfonic groups are grafted to the polymer chain as shown in fig. 1. SPE was applied to electrolytic cell by functioning as an ionic conduction instead of electrolyte solution for tritium enrichment by using electrodes. SPE electrolytic apparatus as shown in fig. 2 can be devided into 4 main parts: SPE cell part, Sample reservoir part, cooling unit part, and Power supply unit.

![Fig. 1 Solid Polymer Electrolyte (SPE) structure](image1)

![Fig. 2 SPE electrolytic apparatus](image2)
**SPE cell part**

The SPE cell part consists of electrolysis unit, shown in fig. 3, which is constructed by porous dimensionally stable anode covered with Titanium chamber and porous stainless steel cathode covered with stainless steel chamber, the SPE membrane is held between two porous metal electrodes. Water is decomposed at the anode generating oxygen gas and hydrogen ions, oxygen gas released passing through the porous anode to anode side reservoir. Hydrogen ions move passing through sulfonic group to cathode and accept electrons become to hydrogen gas releasing to cathode side reservoir. Oxygen and hydrogen are generated separately.

![Diagram of SPE cell part](image)

**Fig. 3 SPE cell part (Electrolysis unit)**

**Sample reservoir part and Cooling unit part**

Water sample is kept in both reservoirs: anode side and cathode side, each reservoir contains 500 ml. the reservoirs are separated but water can pass through the tube inside the electrolysis unit. A cooling unit is installed on the top of each reservoir’s stainless lid to keep the temperature of water vapour down and condense to liquid dropping into the reservoir. The cooling units are set at zero degree centigrade.

**Anode:** \[2H_2O \rightarrow O_2 + 4H^+\]

**Cathode:** \[H^+ + e^- \rightarrow H_2\]
Power supply unit

Power supply provides DC current, 50 ampere and connects to a level sensor which control the final enriched volume constantly at each run. The power is designed to shut off automatically when water level reaches to level sensor.

3. EXPERIMENTAL

3.1 The performance of SPE-1000 prototype

Fifteen electrolysis runs were examined and observed the performance of SPE-1000 during operation. Four items below were observed.

- Electrolysis unit
- Sample reservoir and Cooling unit
- Evaporation and spray loss
- Automatic shut off system

3.2 The fluctuation of concentration factor

The experiments were done for 5 runs by keeping all parameters constant at each run as condition below:

initial volume (Vi) : keep constant at 1000 ml, an error in volume measurement for 1 ml. give a relative error of 0.1 %

final volume (Vf) : keep constant by sensor level control which shut off automatically

initial concentration (Ti) : 0.6 dpm/g approximately

final concentration (Tf) : Tf was measured by LS counting

current : 50.0 A.

counting : Aloka LB III 500 minutes

Teflon vial 100 ml.

water : scintillator (Ultima gold LLT) 50 : 50

Concentration factor (Tf/Ti) was calculated and compared the results.
3.3 Memory effect and Decontamination factor

SPE is a strong acid type cation resin film which contains exchangeable hydrogen atom that tritium can be easy substituted. Their electrodes are porous metals: Anode is porous dimentionally stable anode (DSA), Cathode is porous stainless steel. For those characteristics, enriched water is always maintained in both porous area and tritium is substituted to the exchangeable hydrogen in SPE film as memory effect. A special wash is necessary to decontaminate the system.

At the end of spike runs (standard tritiated water), SPE electrolytic cell is washed by amount of deionized water, background water (tritium-free water), and applied the current of 50 A., for a moment. To determine the memory effect, after decontamination, 1000 ml. of tritium-free water is enriched, measured to obtain the decontamination factor (DF).

3.4 The relationship between concentration factor and initial volume

The theoretical relation of tritium concentration factor versus water volume is expressed in equation 1 as following.

\[
\frac{V_f}{V_i} = \left( \frac{T_f V_f}{T_i V_i} \right)^{\beta_a}
\]

when \(V_f = \) final volume

\(V_i = \) initial volume

\(T_f = \) final tritium concentration

\(T_i = \) initial tritium concentration

\(\beta_a = \) apparent tritium separation factor

The relation in logarithmic scale derived from eq. 1 is

\[
\log(T_f/T_i) = (1-1/\beta_a)\log(V_i) - (1-1/\beta_a)\log(V_f)
\]

When the final volume is kept constant at each run and \(\beta_a\) is apparatus constant, only two independent variables are available, initial volume (Vi) and concentration factor (Tf/Ti). If the relationship between Vi and Tf/Ti in logarithmic scale is plotted by vary the initial volume, a slope is \((1-1/\beta_a)\) and intercept is \(-(1-1/\beta_a)\log(V_f)\).
3.5 Analysis the samples

Two samples were analysed by SPE electrolytic enrichment and compared with the previous analysis which were done by conventional alkaline electrolysis enrichment. The first sample is deep sea water (500 meters in depth) and the second one is surface sea water (1 meter in depth). The samples were measured by Aloka LB III and calculated the tritium content of the original at sampling date by using formula derived from the relationship between concentration factor and initial volume as below:

\[ T_i = \frac{T_f}{10^{(A \log(V_i) + B)}} \]  

(3)

when

\[ A = (1-1/\beta a) \]

\[ B = (1-1/\beta a) \log(Vf) \]

4. RESULTS AND DISCUSSION

The performance of SPE-1000 prototype

SPE part

Many electrolysis runs show that the temperature of both surface electrodes rises up to 50°C during electrolysis making the water hot. After using an electric fan to cool down electrolysis unit, the temperature decrease to 40°C as shown in fig. 4.

Sample reservoir and Cooling part

Sample reservoirs are inspected and found that they have no o-ring seals between reservoirs and their stainless lids causing some water vapour leak from system. Cooling part were not efficient to cool down and condense the water vapour circulating in system. The temperature of the cathode side cooling part was normally higher than the anode side at each run as shown in fig. 4.

The case mentioned above should be improved by the first hand to avoid the effluent from sample leakage.
Fig. 4 Temperature of reservoir's cooling units [Cooling] and electrolysis unit [Electrode] during operation

Run no. SPE-B, SPE-C, SPE-D had no cooling fan.
Run no. SPE-Background (hr. 25) SPE-1500, SPE-2000 were cooled down by cooling fan.
Evaporation and Spray loss

Many electrolysis runs were checked and found that water vapour was trapped by two tube of silica gel moisture absorber about 1.5 - 2.5 gram at each run. Such loss decrease the separation factor. If the electric fan is installed to cool down the electrode, the cooling part of both reservoirs is improved more efficient and o-ring seals added in the system such loss will be controlled and keep minimum.

Automatic shut off system

SPE-1000 prototype use level sensor shutting off power supply automatically when water decreases to sensor level. 15 electrolysis runs showed that the deviation of final volume between runs was within ± 3 ml.

The automatic shut off system of SPE-1000 is not suitable and need to improve for more precision. Amp-hour counter may be a good choice for controlling the final volume constant with high precision.

Counting performance

<table>
<thead>
<tr>
<th>Counter</th>
<th>Aloka LB-III Liquid Scintillation Counter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counting time</td>
<td>50 min. x 20 cycles</td>
</tr>
<tr>
<td>Standard Tritiated water</td>
<td>15194.868 dpm at 9 May 1996</td>
</tr>
<tr>
<td></td>
<td>14158.820 dpm at 15 Aug 1996</td>
</tr>
<tr>
<td>Counting Standard</td>
<td>3653.81 ± 6.07 at 15 Aug 1996</td>
</tr>
<tr>
<td>Background</td>
<td>5.07 ± 0.31 cpm</td>
</tr>
<tr>
<td>Counting efficiency</td>
<td>25.770 %</td>
</tr>
</tbody>
</table>
Table 1 The fluctuation of concentration factor

<table>
<thead>
<tr>
<th>Run no. &amp; ID</th>
<th>Initial volume (V_i) g.</th>
<th>Final volume (V_f) g.</th>
<th>Initial concentration (T_i) dpm/g</th>
<th>Final concentration (T_f) dpm/g</th>
<th>Concentration factor T_f/T_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 SPE-A</td>
<td>998.91</td>
<td>constant</td>
<td>0.5880</td>
<td>4.829</td>
<td>8.81</td>
</tr>
<tr>
<td>2 SPE-B</td>
<td>999.45</td>
<td>constant</td>
<td>0.6020</td>
<td>4.437</td>
<td>7.91</td>
</tr>
<tr>
<td>3 SPE-C</td>
<td>999.24</td>
<td>&gt; 62.7 g</td>
<td>0.6004</td>
<td>4.439</td>
<td>7.93</td>
</tr>
<tr>
<td>4 SPE-D</td>
<td>1000.04</td>
<td>&gt; 65.0 g</td>
<td>0.5803</td>
<td>4.791</td>
<td>8.27</td>
</tr>
<tr>
<td>5 SPE-E</td>
<td>1000.00</td>
<td>&gt; 62.2 g</td>
<td>0.5803</td>
<td>4.976</td>
<td>8.59</td>
</tr>
</tbody>
</table>

Average Concentration factor

8.30 ± 0.40 (% SD) (4.8 \%)  

We expected the main problems of the fluctuation of tritium concentration factor were:
Evaporation loss rate are not constant because of SPE performance.
Automatic shut off system is not efficient to control final volume constant as described.
Dilution error of each standard water is not unity.
Memory effect

The decontamination procedure A

rinse with 300 ml. of deionized water and apply current at 50.0 A. for 5 minutes twice then rinse with 300 ml. of tritium free water and 50.0 A for 5 minutes, dry the water reservoirs, all nozzles and tubes with clean and dried paper.

Table 2A Memory effect & Decontamination factor, using decontamination procedure A

<table>
<thead>
<tr>
<th>Tritium concentration of previous run (Ai) (dpm/g)</th>
<th>Tritium concentration of tritium-free water (Af) (dpm/g)</th>
<th>Decontamination factor (DF) Ai/Af</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.976</td>
<td>0</td>
<td>0.0088</td>
</tr>
</tbody>
</table>

The decontamination procedure B

rinse with 400 ml. of deionized water and apply current at 50.0 A. for 10 minutes twice then rinse with 400 ml. of tritium free water and 50.0 A for 10 minutes, dry the water reservoirs, all nozzles and tubes with clean and dried paper.

Table 2B Memory effect & Decontamination factor, using decontamination procedure B

<table>
<thead>
<tr>
<th>Tritium concentration of previous run (Ai) (dpm/g)</th>
<th>Tritium concentration of tritium-free water (Af) (dpm/g)</th>
<th>Decontamination factor (DF) Ai/Af</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.569</td>
<td>0</td>
<td>0.0110</td>
</tr>
<tr>
<td>0.091</td>
<td>0</td>
<td>0.0030</td>
</tr>
</tbody>
</table>

Memory effect was found in the SPE system. We expected the memory effect was kept in SPE membrane mainly. The porous area of electrodes were the second priority. The decontamination procedure B was examine twice and found that the decontamination factor (DF) of the first wash is 957 and the second is 30. The result showed non-linearity and we expected the relationship between DF and decontamination run to be exponential.
Table 3 The relationship between concentration factor and initial volume [Aloka LB counter]

<table>
<thead>
<tr>
<th></th>
<th>Gross count (cpm)</th>
<th>Net count (cpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG-1</td>
<td>4.760 ± 0.356</td>
<td>(average)</td>
</tr>
<tr>
<td>BG-2</td>
<td>4.728 ± 0.250</td>
<td>4.744 ± 0.435</td>
</tr>
<tr>
<td>SBE</td>
<td>12.844 ± 0.418</td>
<td>8.100 ± 0.603</td>
</tr>
<tr>
<td>STD</td>
<td>3620.18 ± 10.01</td>
<td>3615.43 ± 10.02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ID</th>
<th>Initial volume</th>
<th>Final concentration</th>
<th>Initial concentration</th>
<th>Concentration factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vi</td>
<td>log(Vi)</td>
<td>Bq/l</td>
<td>Bq/l</td>
</tr>
<tr>
<td>SAE-500</td>
<td>500.01</td>
<td>2.699</td>
<td>50.748 ± 0.416</td>
<td>11.682 ± 0.250</td>
</tr>
<tr>
<td>SAE-1000</td>
<td>1000.00</td>
<td>3.000</td>
<td>93.061 ± 0.550</td>
<td>11.692 ± 0.250</td>
</tr>
<tr>
<td>SAE-1500</td>
<td>1500.68</td>
<td>3.176</td>
<td>131.405 ± 0.633</td>
<td>11.683 ± 0.250</td>
</tr>
<tr>
<td>SAE-2100</td>
<td>2099.91</td>
<td>3.322</td>
<td>170.411 ± 0.714</td>
<td>11.669 ± 0.250</td>
</tr>
<tr>
<td>SAE-2500</td>
<td>2500.01</td>
<td>3.398</td>
<td>189.187 ± 0.743</td>
<td>11.658 ± 0.249</td>
</tr>
</tbody>
</table>

The relationship was plotted in the logarithmic scale and shown to be a linear relationship. Using regression, slope calculated to be 0.827 and intercept to be -1.587. The relationship can establish a formula expressed the initial concentration of unknown sample as following.

\[
T_i = \frac{T_f}{10^{0.827 \log(V_i) - 1.587}}
\]

Relationship between Concentration factor and initial volume

![Graph](image)
Table 4 The analysis of unknown samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Tritium content (mBq/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPE electrolytic enrichment</td>
</tr>
<tr>
<td>97 GWHE 24</td>
<td>338 ± 25</td>
</tr>
<tr>
<td>97 GWHE 25</td>
<td>216 ± 24</td>
</tr>
</tbody>
</table>

Comparison the analytical results between SPE enrichment and Alkaline electrolysis method was not corresponding. We can not specify which number is correct, the intercomparison is necessary. However we should be careful the memory effect as mentioned previously, such low-level tritium samples may be affected. Contamination during sampling, storage and preparation is not negligible. Quality control must be considered.

5. CONCLUSION

The SPE-1000 prototype was examined for 15 runs and found very useful for tritium enrichment of water. This enrichment method is more easy and safety than conventional alkaline electrolysis. Especially it was able to reduce the electrolysis time. However, the SPE-1000 prototype is need some improvement for the best performance as described below:

1. Cooling unit part: To cool down and condense the water sample which evaporated and sprayed during electrolysis.
2. Electric cooling fan: To cool down the electrode and electrolysis unit, decrease the temperature of water sample.
3. O-ring: To prevent the leakage of water sample from the sample reservoirs.
4. Automatic shut off system: For precision shut off the current when final volume is fixed at each run.
6. ACKNOWLEDGEMENT

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7. REFERENCES


2. M. Forster, M. Kessler. Low level counting for electrolytically enriched tritium water samples.