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Performance Test of Improved Commercially Available Tritium Enrichment System: Toward Rapid and High Efficiency Enrichment

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A commercially available tritium enrichment system was improved to provide rapid and high efficiency enrichment. Two smaller tanks of double-glazed glass were installed to realize better cooling of sample water at 15 °C. The improved system kept the sample water in the tanks cooler than in the large tanks of the original design. The tritium enrichment factor ranged from 5.24 to 5.50 with the mean value (\pm standard deviation) of 5.40 ± 0.10 and those values were higher than observed for operation before the improvement. The results obtained with the improved system were maintained at a high tritium enrichment factor.

Key words: tritium, enrichment system, high efficiency

1. Introduction

Tritium (^3H ; $T_{1/2} = 12.3$ y) is the only radioisotope of hydrogen and it decays to ^3He . Sources of environmental tritium are natural and artificial. Various reports can be found in the literature which summarize the properties and behaviors of tritium¹⁻⁴. Most of the naturally sourced tritium is produced by the interaction of nitrogen (^{14}N) and oxygen (^{16}O) atoms with cosmic rays in the upper atmosphere, and its production rate has been estimated as 0.25 atoms/cm²/s³, with the global tritium annual radioactivity amount of approximately 72×10^{15} Bq/y⁴.

On the other hand, there are several sources for artificial tritium. Atmospheric nuclear weapon testing from the 1950s to the early 1960s released huge amounts of tritium into the atmosphere in the northern hemisphere, and approximately 1.86×10^{20} Bq of tritium was released from 1945 to 1985⁵. Normal operations of nuclear facilities also release tritium to the surrounding environment, and the annual average discharge rate to the atmosphere worldwide were estimated to be 11.7×10^{15} Bq from 1998 to 2002⁵. Many researchers around the world reported high tritium concentrations in precipitation^{6, 7}. However, by 1996, it was reported that the concentrations had returned to the natural background level⁷.

Since the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident of March 2011, huge amounts of contaminated water have been produced in decontamination and decommissioning work. Although

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the contaminated water has been treated by passing it through the multi-nuclide processing system (ALPS), small amounts of radionuclides, especially tritium which is not removed using ALPS are still present⁸). This treated water is being stored in tanks on site; however, these tanks will soon become full. In response to this, the Japanese government approved a plan on 13 April 2021 to release the stored treated water including mainly tritium from the site to the Pacific Ocean⁹). In the future, tritium monitoring will be conducted by the Tokyo Electrical Power Company Holdings, the Ministry of Environment, the Fukushima Prefecture government, and others. Regarding the marine environmental monitoring for ALPS treated water to be conducted by the Japanese government, the lower detection limit target for tritium was set at 0.1 Bq/L each for seawater and tissue free water tritium (TFWT), while organically bound tritium (OBT) of aquatic organisms was set at 0.5 Bq/L-combustion water¹⁰).

In general, low level tritium concentration in environmental water samples is measured using large vials of 145 mL and a low background liquid scintillation counter (LSC) for 1,000 min with a minimum detection limit of approximately 0.3 Bq/L¹¹). To detect less than 0.3 Bq/L of tritium in water samples, tritium has to be enriched using an additional procedure. In Japan, a tritium enrichment system using a solid polymer electrolysis (SPE) membrane is commonly used, which has less danger of explosion due to the separation of the exhausted H₂ and O₂ during the tritium enrichment¹²). It has been reported that it is possible to detect tritium concentrations of approximately 0.04 Bq/L using a procedure in which 800 mL of sample water is concentrated using this device for approximately 3 days and measured using LSC for 1000 min¹³⁻¹⁶). For safe and rapid tritium monitoring in the marine environment, a higher-performance tritium enrichment system is needed. It has been reported that electrolysis of a water sample under low temperature conditions is effective in obtaining a high separation coefficient¹⁷). Akata *et al.*¹⁸) took on the challenge to get high performance enrichment with a low volume sample of 500 mL under the cooling condition using double glass reservoirs equipped with a cooling water circulation device. They obtained a tritium enrichment factor of 5.00 which is higher than normally obtained. However, there is still ample room for improvement for such points as the size of the tanks in the SPE setup. It is important also to shorten the time to obtain analytical results on the released concentrations of tritium to dispel rumors about damage to the marine environment. This paper reports on the performance improvement of the commercially available system to make it faster and more efficient.

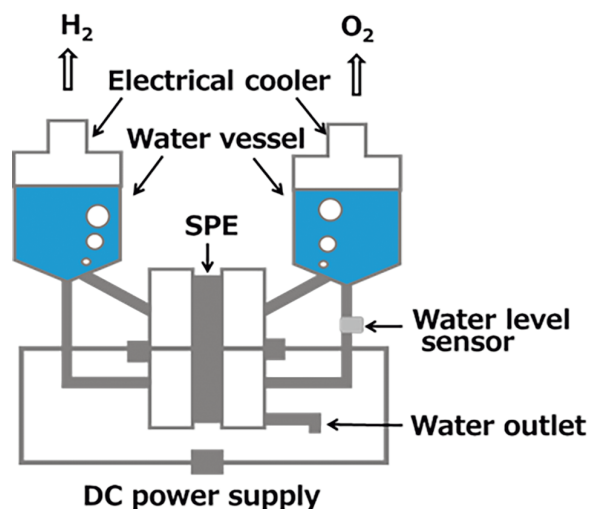


Fig. 1. Schematic diagram of the commercially available electrolytic apparatus "TRIPURE" with the solid polymer electrolysis (SPE).

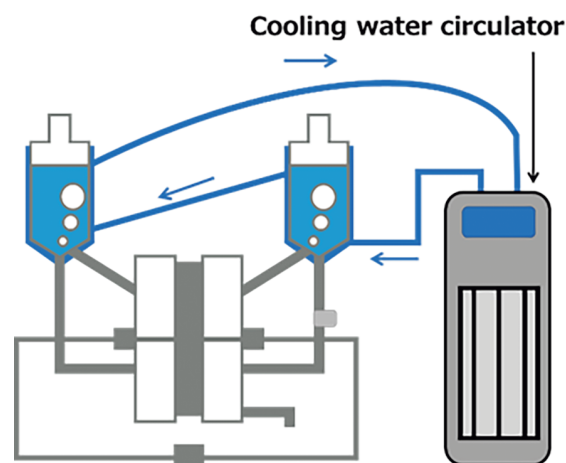


Fig. 2. Improved SPE system with small double-glazed glass tanks connected to the cooling water circulator.

2. Experimental

2.1. Overview of apparatus

In this study, the "Tripure" (XZ001, De Nora Permelec Ltd. Japan) was improved which is a commercially available SPE membrane electrical tritium enrichment system (Fig. 1). Its details have been reported previously^{12, 18}). Briefly, it consists of two water tanks with Peltier type electrical coolers, the electrolysis cell and a DC power supply. The electrolysis cell is composed of an SPE membrane made of fluorocarbon resin, a porous anode made of porous Ti coated with iridium oxide and a porous cathode made of SUS316. The electrolysis was started at a constant current of 50 A until the water volume was

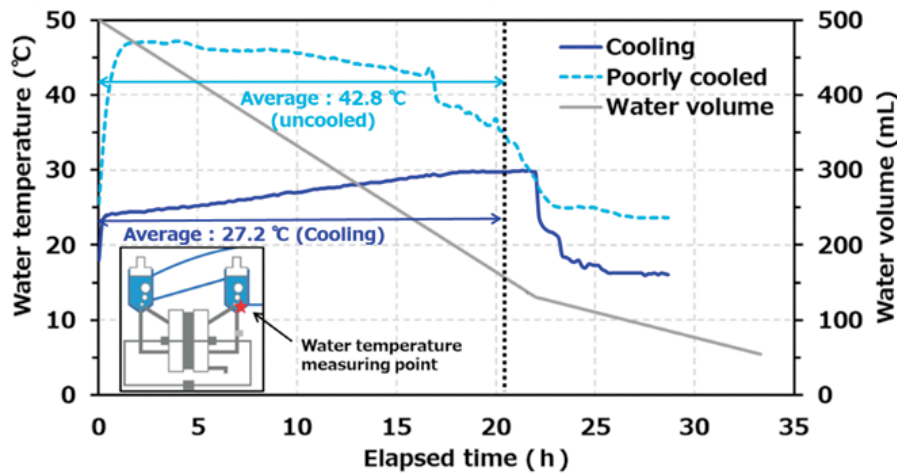


Fig. 3. Sample water temperature and volume during the cooled and poorly cooled enrichment experiments. The vertical dashed line indicates the 22 h time limit for switching to the lower applied current.

reduced to approximately 100 mL and then electrolysis was done at 20 A to reach the top of the water level sensor and get a volume of about 52 mL¹²⁾. Akata *et al.*¹⁸⁾ reported that a somewhat higher efficiency was observed when the same size of tanks (approximately 1,000 mL per tank) which were made of double-glazed glass were used in place of the single-glaze glass tanks that had no gap to allow cooling water to be circulated for better cooling (Tripure-1). It seems that the enrichment factor depends on the performance of the electrolytic membrane. In other words, the cooling efficiency of the sample water is determined by the contact area between the cooling area and the sample water. Then, an additional improvement was realized. Two smaller tanks (approximately 360 mL per tank) of double-glazed glass were installed for better cooling of sample water. Figure 2 shows the improved enrichment system (Tripure-2). The cooling water temperature of the circulator (CCA-1110, EYELA, Japan) was set at 15 °C which was considered to be the laboratory temperature. The sample water temperature was determined using a thermo recorder (TR71nw, T&D, Japan).

2.2. Calculation of tritium enrichment factor

The relationship between tritium concentration in sample water and water volume during electrolysis is defined by the following equation,

$$\frac{V_f}{V_i} = \left(\frac{T_f \times V_f}{T_i \times V_i} \right)^\beta \quad (1)$$

where T_i and T_f are initial and final tritium concentrations, and V_i and V_f are initial and final water volumes, respectively. β is the separation factor of tritium. The separation factor β is influenced mainly by the isotope

fractionation due to evaporation, the inside pressure of the electrolytic cell, and the vapor pressure of sample water during electrolysis. So, it is common to determine an apparent separation factor β_a experimentally. The tritium enrichment factor Z_T is defined using the following equation.

$$Z_T = \frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{\left(1 - \frac{1}{\beta_a}\right)} \quad (2)$$

In general, operation time of electrolytic enrichment technique of tritium depends on the initial water volume and electric current value. Total enrichment time from 500 mL was less than 28 h. The D₂O reagent (Sigma-Aldrich, USA) was diluted using pure water to prepare the secondary tritium standard solution-A which was 4.14 ± 0.09 Bq/L ($n = 5$) for determining the tritium enrichment factor.

2.3. Tritium measurement

The water sample (50 mL) was mixed with 50 mL of a liquid scintillation cocktail (Ultima Gold LLT, PerkinElmer, USA) in a 145 mL low diffusion polyethylene vial with an inner Teflon coating. Tritium concentration was measured using a low background liquid scintillation counter (LSC-LB5, Nippon RayTech, Japan) for 1,000 min (50 min \times 10 repeats \times 2 cycles). Counting efficiency was determined using secondary tritium standard solution-B of 118.17 ± 0.39 Bq/L (reference date: 9 September 2020) produced by D₂O reagent (Sigma-Aldrich, USA)¹⁶⁾. The minimum detection level was calculated as approximately 0.3 Bq/L.

Table 1. The estimated tritium enrichment factor of the un-cooling and cooled enrichment experiments

Number	Un-cooling experiment	Cooling experiment
1	4.55	5.50
2	4.35	5.43
3	4.86	5.38
4		5.24
5		5.42
Ave. (\pm S.D.)	4.59 \pm 0.26	5.40 \pm 0.10

3. Results and discussion

3.1. Cooling effect using small tanks

Figure 3 shows the sample water temperature and water volume during the enrichment process using the improved enrichment system. Until the volume reached about 100 mL, the average water temperature using the cooling water circulator was 27.2 °C and lower than the average water temperature of 42.8 °C in the poorly cooled experiment. The average water temperature was approximately 15 °C lower. The Tripure-2 effectively cooled the sample water in the tanks.

3.2. Evaluation of tritium enrichment factor Z_T

The tritium enrichment factor Z_T was determined three times for un-cooling experiment and five times for the cooling experiment. Table 1 summarizes the values of Z_T . Although tritium enrichment factor using Tripure-2 under un-cooling condition ranged from 4.35 to 4.86 with mean value (\pm standard deviation) of 4.59 \pm 0.26 ($n = 3$). On the other hand, tritium enrichment factor using same system under cooling condition by cooling water circulator (15 °C) ranged from 5.24 to 5.50 with mean value (\pm standard deviation) of 5.40 \pm 0.10 ($n = 5$). These data points suggested that the enrichment process was reasonably stable under the cooling condition with the water circulator providing cooling water in the gap of the double-glazed glass. Akata *et al.*¹⁸⁾ reported that a tritium enrichment factor of 5.00 was gotten under the cooling condition using almost the same volume of tanks (approximately 1,000 mL per tank) and this was higher than Z_T for normal operation. The Tripure-2 which had small tanks and water cooling in the gap provided higher efficiency than Tripure-1 and the previously reported improved system¹⁸⁾. It seemed that the smaller size of the tanks was effective for increasing the contact time between the sample water and tanks, thereby keeping the water temperature lower. Therefore, it was presumed that the high enrichment factor was obtained in a short enrichment time using a small initial volume of sample water. The minimum detection level using the Tripure-2 at an initial volume of 500 mL and LSC counting time of

1,000 min was estimated to be approximately 0.056 Bq/L which was lower than the value for normal “Tripure” operation (0.065 Bq/L). The relatively uncertainty of this procedure was calculated approximately 8 %. Ueda *et al.*¹³⁾ reported that an enrichment factor of 7 to 8 was observed using 800 mL of water as the initial volume, and the operation time was about 50 h. The operation time of Tripure-2 was approximately 28 h.

Tritium concentration level in natural water has been reported elsewhere¹⁹⁻²¹⁾. Recently, the most important target among environmental media is the tritium concentration in sea water and marine products. The lower detection limit target for tritium was set at 0.1 Bq/L for marine environment monitoring by the Japanese government¹⁰⁾. Monitoring data should be made available to researchers as well as the general public as quickly as possible. Here, if the minimum detection level of tritium measurement is approximately 0.3 Bq/L, Z_T has to be 3 or higher. Additionally, high tritium enrichment factor and stable enrichment operations are also important for getting low uncertainty of tritium measurement.

4. Conclusion

The commercially available “Tripure” tritium enrichment system was improved to achieve faster and higher efficiency of enrichment. Two small tanks (approximately 360 mL per tank) of double-glazed glass were installed for cooling of sample water at 15 °C by circulating water through the gap of their double-glazed glass structure. The improved system kept the sample water in the tanks cooler than the normal system with polyethylene tanks that had no gap cooling. The tritium enrichment factor Z_T ranged from 5.24 to 5.50 with the mean value (\pm standard deviation) of 5.40 \pm 0.10. The improved system was operated stably at high Z_T . For monitoring of the marine environment, the improved system offered time savings of about 24 h compared to the normal one and Tripure-1.

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Conflict of interest disclosure

The authors declare that no conflict of interest exists.

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