Note

Low-volume Electrolytic Enrichment for Tritium Measurement Using Improved Solid Polymer Electrolyte System at NIFS and Its Application

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We evaluated the enrichment factor of tritium for an improved solid polymer electrolyte (SPE) system. In this system, water sample reservoirs were made of double-glazed glass, and cooling water was circulated in the double glass to cool the sample. As the result, a tritium enrichment factor of 5.00 was obtained and the MDL of tritium measurement with a low-background liquid scintillation counter coupled to this improved enrichment process was determined to be approximately 0.062 Bq L^{-1}. Tritium concentration in monthly precipitation at Kumamoto was measured using this method combining a low-background liquid scintillation counter and this improved SPE system.

Key words: tritium, electrolytical enrichment, low volume

1. Introduction

Tritium (^{3}H; $T_{1/2}$ = 12.3 y) is the radioisotope of hydrogen and it decays to ^{3}He[1]. Most natural tritium is produced through the interaction of secondary cosmic rays with nitrogen and oxygen atoms in the upper atmosphere [2]. On the other hands, atmospheric nuclear weapon testing during 1950s to 1960s released significant amounts of tritium into the environment. As the result, tritium concentrations in precipitation rapidly increased in the world. After the nuclear weapon tests were stopped, the concentration level was gradually decreasing, and almost returned to background level. Recently, nuclear facilities have become the dominant anthropogenic source. After the Fukushima Dai-ichi Nuclear Power plant accident, slightly high tritium concentrations were observed in

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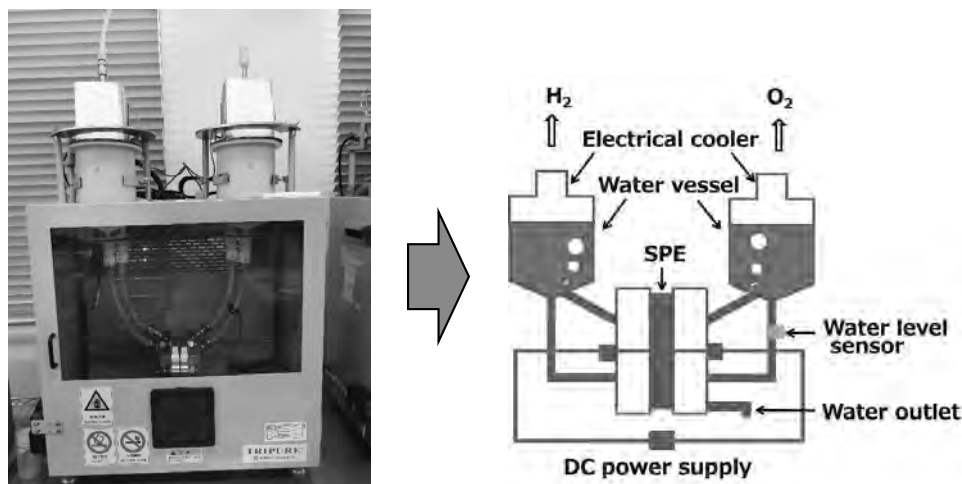E-mail: akata@hirosaki-u.ac.jp

Fig. 1. The commercially available SPE electrolytic apparatus "Tripure"

environmental samples compared to the background level[3]. It is known that background tritium concentration in the general environment in Japan is dependent on local geographical condition[4, 5]. For example, Akata *et al.* reported tritium concentration in monthly precipitation collected at Rokkasho village and Chiba city. Although the observed peak concentrations at Chiba were in similar periods at Rokkasho as well, the former had lower values than the latter[6]. The peak concentration is considered to be controlled by the air mass arriving from the Asian continent to the observation site (continental effect and dilution effect by sea water). On the other hands, the deuterium plasma experiments using LHD were started at National Institute for Fusion Science since March 2017, and a small amount of tritium was produced by a fusion reaction in the deuterium plasma experiment[5]. Therefore, it is important to understand the background tritium concentration level in environment in Japan. In general, the tritium concentration in environmental water samples were measured using a low background liquid scintillation counter. However, the lowest detection limit is approximately 0.3 Bq L^{-1}, and some samples were lower than detection limit[6]. Therefore, it is necessary to use an enrichment process for the precise measurement of tritium using a low background liquid scintillation counter. The conventional method for tritium enrichment has disadvantageous points, namely the potential danger for explosion by hydrogen gas and an enrichment limitation due to an increase of alkali concentration with progress of electrolysis. Recently, the Solid Polymer Electrolysis (SPE) became developed, which has less danger of explosion due to the separated exhaust of H_2 and O_2 during tritium enrichment[7, 8]. On the other hand, the required initial volume is approximately 1000 mL[9], and

small volumes, like under 500 mL, cannot be processed by this method. In this paper, the SPE system was improved for high separation factor, and monthly precipitation samples collected at Kumamoto were processed using this improved system to prove its application.

2. Experimental

2.1 Overview of improved SPE system
A commercially available electrolytic apparatus named "Tripure" (XZ001, De Nora Permelec Ltd. Japan) shown in Figure 1 was used. An overview of SPE device has already been reported[7–9]. It consists of two water reservoirs with Peltier type electrical coolers, the electrolysis cell and a DC power supply. The electrolysis cell is composed of solid polymer electrolytic film made of fluorocarbon resin, a porous anode made of coated with iridium oxide on porous Ti and porous cathode made of SUS316. It is a safe system, with less explosion risk, due to the separated exhaust of H_2 and O_2 gases. It has been reported that electrolysis of the water sample at low temperature conditions is effective for obtaining a high separation coefficient[10]. So, the water reservoirs were modified to double glass reservoirs and cooling water was passed through the double glass to lower the temperature of the sample water. The picture of improved system is shown in Figure 2.

2.2 Tritium enrichment factor determination
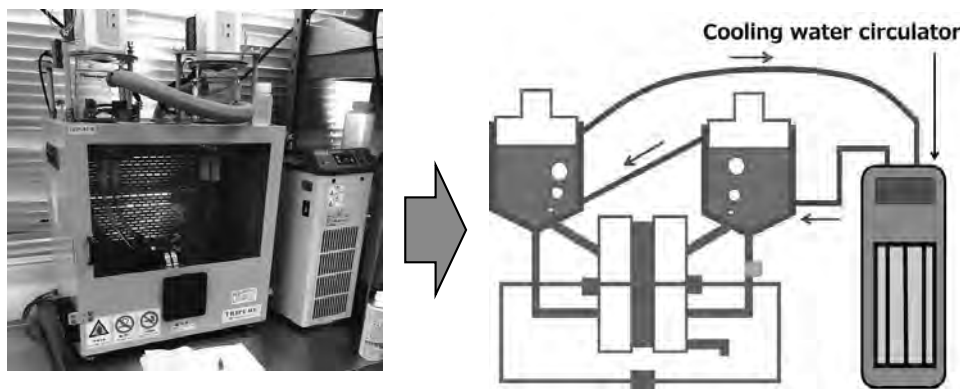The relationship between tritium concentration and water volume during electrolysis is defined by the following equation[1]:

Fig. 2. The Improved SPE system with double glass tanks connected to a cooling water circulation device

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

where V_i and V_f are initial and final water volumes, T_i and T_f are initial and final tritium concentrations, respectively. β is separation factor of tritium. Usually the separation factor has been influenced by some effects, for example, isotope fractionation due to evaporation, inside pressure of the electrolytical cell, vapor pressure of sample water during electrolysis, etc. Therefore, it is common to determine apparent separation factor, β_a, by an experiment. And tritium enrichment factor (Z_T) is defined using the following equation.

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

In this experiment, the initial water volume of the SPE device was set to 500mL. The electrolysis was done at a constant current of 50 A for 22 hours and 20 A until the final volume of sample reached approximately 55 mL. The cooling water temperature was set at 15℃ which is lower than the laboratory temperature throughout the year. The 50 mL of water sample 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 radioactivity was measured with a low background liquid scintillation counter (LSC-LB7, Hitachi, Japan) for 1,500 min. Counting efficiency was determined using tritium standard water (SRM 4361C, NIST, USA). The typical background count rate and counting efficiency were approximately 2.8 cpm and 22%, respectively. The minimum detection level was approximately 0.31 Bq L^{-1} [11]. The D$_2$O reagent (Sigma-Aldrich, USA) was diluted using pure water to prepare the secondary tritium standard solution which is 2.16 ±

Table 1. Tritium enrichment factor of improve aperture

Run	Final concentration (Bq L^{-1})	Tritium enrichment factor (Z_T)
1	10.94 ± 0.15*	5.07
2	10.85 ± 0.15	5.02
3	10.61 ± 0.16	4.91
4	10.75 ± 0.15	4.98
5	10.79 ± 0.15	5.00
Ave	10.79 ± 0.12	5.00 ± 0.06**

*Counting error
**Standard Deviation

0.09 Bq L^{-1} (n = 5).

3. Results and Discussion

3.1 Evaluation of enrichment factor

The evaluation experiment to determine the apparent enrichment factor was performed five times. Table 1 shows the summary of the evaluation experiments. Final tritium concentration ranged from 10.61 to 10.94 Bq L^{-1}, and the mean value (±Standard deviation) is 10.79 ± 0.12 Bq L^{-1}. These data points agree well with each other, it suggesting that the electrolysis process was stable under our laboratory conditions. The experiment was also carried out without the cooling water circulator (under room temperature conditions), and the final tritium concentration was 9.44 ± 0.15 Bq L^{-1} (n = 1), which is lower than that obtained under cooling. This result was similar to other report by Uematsu *et al.*[10], and low temperature conditions result in a better enrichment factor than without controlling the temperature of sample water. The calculated average tritium enrichment factor (Z_T) with standard deviation is 5.00 ± 0.06 (Z_T of before improved system: 4.37). Using this result, the MDL of tritium measurement coupled electrolytic enrichment procedure under this condition is estimated to be approximately

0.062 Bq L^{-1} (MDL of before improved system: 0.071 Bq L^{-1}) using reported method[12].

3.2 Tritium concentration in monthly precipitation at Kumamoto

After the tritium enrichment factor of our improved solid polymer electrolyte system was determined, it has been applied to measure precipitation samples. Monthly precipitation samples were collected at Kumamoto University (32.48'48"N, 130.43'45"E), Japan using a rain sampler (Rain Sampler RS1, Palmex ltd., Croatia). Approximately 600mL of precipitation samples were distilled, and 500 mL of distilled water sample was electrolyzed to a volume of 55 mL. Tritium concentration was measured by the method described above. Figure 3 shows the seasonal variation of tritium concentration in monthly precipitation at Kumamoto together with the reported values of Kumamoto from the IAEA database[13]. Some samples could not be analyzed due to their small collected volume (December 2017 and November 2018). The tritium concentration in monthly precipitation at Kumamoto from August 2017 to July 2019 ranged from 0.19 to 0.52 Bq L^{-1} with the mean value ($\pm$ standard deviation) of 0.28 $\pm$ 0.09 Bq L^{-1}. Concentrations reported by IAEA from April 2015 to January 2016 ranged from 0.12 to 0.32 Bq L^{-1}. Our data were comparable to the reported values from IAEA. Momoshima *et al.* (2008) reported that tritium concentration in individual precipitation at Kumamoto city during 2001 to 2006 ranged from 0.11 to 1.04 Bq L^{-1} [14], which is slightly higher than those in the present study. This result is probably due to the environmental half-life. The seasonal trend for tritium concentration in precipitation was similar to the general background pattern observed in Japan, which is high in spring and low in summer[15].

4. Conclusion

A commercially available solid polymer electrolysis (SPE) system was improved for high separation factor using double glass reservoirs equipped with a cooling water circulation device. As the result, a tritium enrichment factor of 5.00 was obtained, which was higher than normal operation without cooling. The MDL of tritium measurement coupled with low-background liquid scintillation counter with this improved enrichment process was estimated to be approximately 0.062 Bq L^{-1}. In addition, tritium concentration in monthly precipitation were studied using this application. In future, we plan to use this procedure to understand the background tritium concentration level in environmental water.
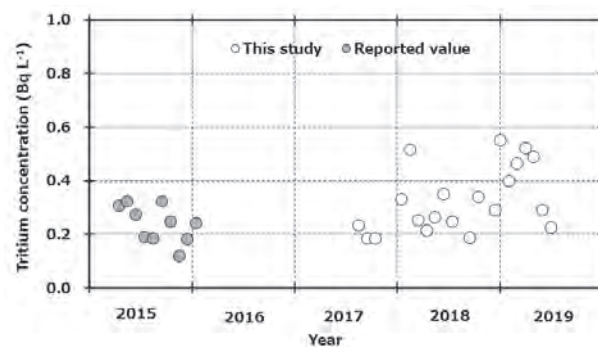

Fig. 3. Tritium concentration in monthly precipitation collected at Kumamoto, Japan.

Conflict of interest disclosure

The authors declare no conflicts of interest.

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