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RESEARCH ARTICLE

FUNDAMENTAL STUDIES ON THE ENRICHMENT OF ^3H IN WATER USING FREEZING AND MELTING POINT DIFFERENCES OF H_2O AND T_2O .

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Abstract

The method we proposed using their boiling point differences are processed during the vacuum distillation, thus was expected to reduce the enrichment processing time, however it was not effective in enriching ^3H . For the method using their melting point differences, we set a beaker of solidified ^3H containing water at around $1\text{ }^\circ\text{C}$ and let the ice liquefy. We assumed the portion liquefied first was H_2O (melting point at $0.00\text{ }^\circ\text{C}$) and the remaining portion in the beaker had enriched ^3H . This remaining portion was collected in a vial and its ^3H concentration was measured. The remaining portion contained 1.10 times more ^3H than before the procedure, showing a small enrichment effect. Our future research will focus on improving the enrichment factor.

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Introduction:-

Tritium (^3H or T) is a radioactive isotope of hydrogen. Its nucleus is consisted of one proton and two neutrons, i.e., having the mass number of three. In nature, tritium is formed by nuclear reaction of nitrogen or oxygen in the atmosphere with neutrons or proton of the cosmic ray with the formation rate of about $0.2\text{ tritium}/\text{cm}^2/\text{s}$. Tritium formed by the cosmic ray are keeping an equilibrium state of forming and decaying with its amount about $1\text{--}1.3 \times 10^{18}\text{ Bq}$ on Earth ⁽¹⁾. However, ^3H generally measured in the environment are “fallout tritium”; large amount of ^3H emitted to the environment from the past nuclear testing and “facility generated tritium”; ^3H released to atmosphere and ocean with control from nuclear facilities such as nuclear power plants and nuclear fuel reprocessing facilities.

H forms tritiated water (HTO or T_2O) by reacting with oxygen. It exists on Earth as a mixture with light-water (H_2O) and spread out widely in the form of vapor, precipitation, ground water, ocean water, drinking water, and in living organisms. Tritiated water has similar chemical properties as light-water. Thus, it is easily taken into human bodies and be a potential cause of internal exposure. ^3H has been considered as one of the most harmless radioactive nuclides having small influences on humans and animals because it spreads out in the body evenly, has short biological half-life (about 10 days), and has low β -ray energy ^{(2), (3)}. On the other hand, some reports β -ray

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damages animal cells and “transmutation” of ^3H to ^3He destroys biomolecules ⁽³⁾. For example, two production workers who handled a large amount of ^3H died from internal exposure ⁽⁴⁾.

Japanese people’s concerns on radioactive materials have increased after the accident of Fukushima Daiichi Nuclear Power Plant caused by Tohoku Pacific Ocean Earthquake. It increased people’s anxiety and fear levels living near nuclear plants. Despite of the public concerns, most nuclear plants in Japan have restarted its operation or are in the process of restarting. ^3H produced at nuclear plants are released to surrounding area with control. Most likely, ^3H found in the ocean near nuclear plants has higher concentration than in other areas. However, normal ^3H concentration in most ocean is in low Bq/L ^{(5), (6)} and for the accurate measurement of ^3H requires sample enrichment. Therefore, we evaluated the enrichment method that has been widely used and discussed the possibility of developing new enrichment methods using melting point, boiling point, and vapor pressure differences of H_2O and T_2O .

Material And Methods:-

Purification of water sample by vacuum distillation:-

Radiation emitted from ^3H is measured by a liquid scintillation counter (LSC). The presence of impurities such as salt in the water sample prevents the complete mixing of the sample with liquid scintillator and causes dual phase separation. Thus, the sample needs to be purified before mixing with the liquid scintillator. To purify the sample, atmospheric or vacuum distillation methods are generally used.

Reduced pressure used for vacuum distillation enables using a lower temperature for distillation than with the atmospheric method. This allows to distill samples having high boiling point or samples that decompose at high temperatures. Also, it reduces the distillation time.

In this work, we focused on vacuum method and optimized parameters for the sample pretreatment (water bath temperature, pressure settings, cooling water temperature, distillation water to sample ratio, and distillation time). The distillation water to sample ratio and distillation time are influenced largely by water bath temperature and vacuum settings of aspirator (DAS-01: Labotechno Co. JAPAN) and cooling temperature of thermos circulator (THERMO CIRCULATOR ZL-100: TAITEC Co. JAPAN). Thus, the optimized parameter settings will be decided based on observed distillation water to sample ratio and the distillation time. Tap water was used as the test sample for the optimization. Using tritium analysis method ⁽⁷⁾ as a reference, we performed below steps for the optimization.

1. Fig.1 shows the apparatus setting. 100 mL of the test sample was transferred into an eggplant-shape flask. To prevent damaging the glass from rotary evaporator (RE-200: YAMATO Co. JAPAN), boiling chips were not added.
2. Collected distilled water in a round-bottom flask and distilled the sample until it was completely or nearly dried.
3. Table 1 shows various parameter combinations tested. Distillation water to the sample ratio and the distillation time were calculated for each combination and from the result, the optimized parameter was decided.

Sample enrichment:-

The most often used method for the enrichment of tritiated water is electrolytic enrichment using solid polymer electrolyte (SPE) ^{(8), (9)}. Unlike electrolysis using acid or alkaline, SPE electrolysis enrichment allows the enrichment of pure water. It is advantageous because of its simplicity in separating the generated gas, and thus has lower risk of explosion. However, the apparatus that offers high enrichment capacity or the one simultaneously handles large amount of sample are very expensive. The apparatus with lower prices have disadvantages of long distillation time and higher running cost owing to its electricity use. We compared SPE electrolysis enrichment and other enrichment methods in this study.

Sample enrichment by SPE electrolysis:-

Fig 2. shows the apparatus setting of SPE electrolysis used in the study (Electrolyser 10: H-Tec Education, Germany). Following steps were performed for the measurement.

1. 60 mL of the test sample was added to the storage tanks. We used 300 Bq/mL tritiated water to make the enrichment factor calculation easy.
2. Connect the electrolyser to a DC power supply (PMC18-5: KIKUSUI ELECTRONICS Co., JAPAN) and applied max allowable voltage at 4 V and max allowable current at 2 A to enrich the sample until the volume of the liquid is halved from its original (about 48 hours).

- Mix the enriched sample and emulsified scintillator (ULTIMA GOLD™ LLT: PerkinElmer, Inc. USA) in a vial and then measure ^3H radiation by LSC (LSC-5100: Hitachi, Ltd. JAPAN) for 10 min.

Sample enrichment using boiling point differences of H_2O and T_2O under vacuum distillation:-

This enrichment method uses the difference in boiling points of light-water and tritiated water. It has an advantage of reducing the sample pretreatment time as this enrichment is processed during the vacuum distillation to remove salt and other impurities in the ocean water. Table 2 shows boiling points of H_2O , heavy-water (D_2O), and T_2O ⁽¹⁰⁾. Test sample used here was the same as the one used in 2.2.1(1), i.e., 300 Bg/mL tritiated water. Following steps were taken.

- Distillation was performed until the sample volume inside the eggplant-shape flask was halved from the original. Collect the distilled water in the round-shaped flask and count this as one distillation.
- Add sample with the same amount of liquid as the collected portion into the eggplant-shape flask and repeat the distillation steps.
- For both third and fifth distillations, distill the sample until the eggplant-shape flask becomes completely empty. Transfer the distilled water to a measuring vial and measure ^3H radiation by LSC.

Sample enrichment using melting point differences of H_2O and T_2O under vacuum distillation:-

Table 1 shows melting points of H_2O , D_2O , and T_2O . The melting point difference between H_2O and T_2O is $4.49\text{ }^\circ\text{C}$, which is larger than their difference in boiling points (1.15°C) and this fact is well known ^{(10), (11)}. Therefore, we considered developing an enrichment method using their melting point difference. The method used is described below.

- 100 mL of tritium water with known concentration was transferred into a Teflon beaker and the water was solidified in a freezer. The Teflon beaker was wrapped with styrene foam to slowly solidify the water to prevent the ice to have clouded center.
- Transfer the beaker to a water bath of about $1\text{ }^\circ\text{C}$ and let the ice to melt slowly. Cover the beaker top with a piece of aluminum foil to prevent the sample from evaporating, i.e., to prevent ^3H concentration to change.
- Based on their melting points, consider the first portion melted is mainly H_2O and the solid portion left in the beaker is mainly T_2O . Measure each portion by LSC.

Results And Discussion:-

Optimization of sample purification and its parameters by vacuum distillation:-

Table 3 shows the optimal settings obtained for the vacuum distillation. Conductivity of the sample before and after the distillation was measured by a conductivity meter (DiST5: Sansyo Co., Ltd. JAPAN). The conductivity of the test sample (tap water) before the distillation was about $140\text{ }\mu\text{S/cm}$ and after the distillation was about $5\text{ }\mu\text{S/cm}$. Conductivity of pure water prepared by commercially available water purifying system is required to be less than $10\text{ }\mu\text{S/cm}$ ⁽⁷⁾, and thus the distillation method we used served the purpose of purification.

As for the water bath temperature setting, higher temperature settings may cause explosive boiling, but lower temperature settings may elongate the distillation time. Explosive boiling may also occur when the system pressure and the water bath temperature are not well controlled. The conditions we used in this experiment was consistent with the vapor pressure curve for water ⁽¹²⁾, thus it was considered as a suitable parameter for the study.

Electrical conductivity ($\mu\text{S/cm}$) shows material's ability to conduct an electric current. If a solvent contains a large number of electrolytes such as dissociated ions, it has smaller electronic resistance, and thus easier to conduct electricity. In contrast, if a solvent contains a small number of electrolytes, it is difficult to conduct electricity. Pure water, H_2O , dissociate into H^+ ions and OH^- ions, but because of its very low dissociation constant, most H_2O does not dissociate and results in having very low electrical conductivity. Table 4 shows the electric conductivity of the distilled water processed by the vacuum distillation. Based on this measurement, the processed water met the purity level of pure water.

Sample enrichment by SPE electrolysis:-

Table 5 shows the time taken for the electrolytic enrichment and the measured LSC values. The enrichment factor we achieved using the SPE electrolyzer for two days was 1.66. This method is easy as electrolytic enrichment can be applied directly to purified water. However, as the electrolytic enrichment proceeds, temperature of the metal electrodes increase and the conductivity of the electrode decrease. Thus, to increase the enrichment factor, it requires

to cool the apparatus. Moreover, electronic enrichment is a technique using the production rate differences of H₂ gas and T₂O gas. This means, the fluctuation of the production rate follows Maxwell-Boltzmann distribution⁽¹³⁾, resulting in spreading T₂O gas, and thus releasing tritium into the environment in some level⁽¹⁴⁾.

Sample enrichment using boiling point differences of H₂O and T₂O under vacuum distillation:-

Table 6 shows the measured LSC values of the enriched samples. ³H radiation measured before the enrichment, after 3rd and after 5th distillation were 8351.2 cpm, 8355.7 cpm, and 8349.3 cpm respectively. The final enrichment factor was 1.00. The differences in their results were within the systematic error, and thus indicates that there was no enrichment of the sample. Repeating multiple distillation steps did not improve the enrichment factor. It is possible since the water bath used in this experiment was not feasible to give fine adjustments, thus both light-water and tritiated water evaporated at the same time. Also, considering the apparatus' limited settings, it is difficult to control the small temperature difference of 1.4 °C. Therefore, we concluded that this enrichment method was not effective.

Sample enrichment using freezing point and melting point differences of H₂O and T₂O:-

Table 7 shows the measured LSC values. The enrichment factor obtained for the method using freezing point difference was 1.10. The method uses the temperature differences of T₂O and H₂O's freezing and melting points. Freezing starts from the inside wall of the beaker and the sample surface. Most T₂O solidifies before H₂O does. In contrast, H₂O starts liquefying before T₂O does. The method we used in this study was to solidify the sample in a freezer and then liquefy it at 1°C. In general, since the liquefaction starts from the solid surface, the enrichment factor tends to be low. To improve the enrichment, another solidification method was proposed: Set a small metal cooling ball such as a handy cooler in the center of sample surface. Solidify the sample at a temperature between the freezing points of T₂O and H₂O. This allows T₂O that contains large amount of ³H to solidify around the metal cooling ball. Thus, the portion solidified near the metal cooling ball contains highly concentrated ³H and the solidified portion on the other part of ice surface contains high H₂O. Under this condition, liquefaction starts from the solid surface containing high H₂O, results in expecting a higher enrichment factor for ³H.

Table 1:-Each parameter and setting range

Parameter	Setting range
Water bath temperature	60~80 °c
Vacuum settings of aspirator	70~100 kPa
Cooling water temperature	5~15 °c

Table 2:-Boiling point and melting point H₂O, D₂O, T₂O at 1 atm [°c]

	H ₂ O	D ₂ O	T ₂ O
Boiling point	100.00	101.74	101.51
Melting point	0.00	3.82	4.49

Table 3:-The optimal settings obtained for the vacuum distillation

	Setting range	Optimal setting
Water bath temperature	60~80 °c	About 70 °c
Vacuum settings of aspirator	70~100 kPa	About 85 kPa
Cooling water temperature	5~15 °c	10 °c
Recovery rate		About 95 %
Distillation time		About 1 hour

Table 4:-The electric conductivity of the distilled water processed by the vacuum distillation [μS/cm]

Before distillation	After distillation
140 ± 20	5 ± 1

Table 5:-The time taken for the electrolytic enrichment and the measured LSC values

	Sample water volume [ml]	Electrolytic enrichment time [hour]	LSC values [cpm]	Enrichment factor
Before	60	48	8351.2 ± 19.2	1.66

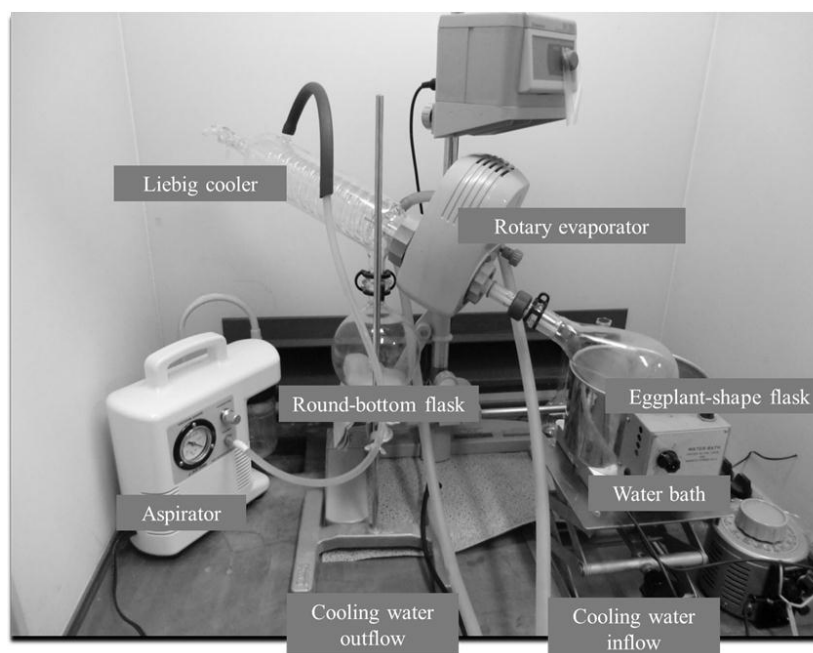
electrolytic enrichment			
After electrolytic enrichment	35		13853.5 ± 39.2

Table 6:-The measured LSC values of the enriched samples [cpm]

	LSC values [cpm]	Enrichment factor
Before distillation	8351.2 ± 19.2	—
Single distillation	8359.8 ± 28.3	1.00
3 th distillation	8379.0 ± 29.1	1.00
5 th distillation	8347.3 ± 26.4	1.00

Table 7:-The measured LSC values of enrichment using freezing point and melting point differences of H₂O and T₂O

	LSC values [cpm]	Enrichment factor
Before enrichment	7922.7 ± 15.5	1.10
After enrichment	8692.3 ± 27.9	

**Figure 1:-**The apparatus setting of vacuum distillation

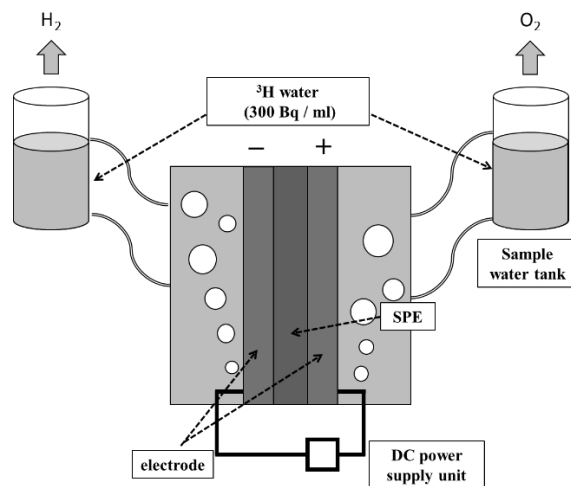


Figure 2:-The apparatus setting of SPE electrolysis.

Conclusion:-

The enrichment methods compared were SPE electrolytic enrichment (the method most often used) and enrichment methods using the differences in freezing, melting, and boiling points of H_2O and T_2O . The new method using the differences of freezing and melting points of H_2O and T_2O achieved an enrichment factor of 1.10 and showed its potential for the future use. The method we developed retains the tritium in the sample opposed to the SPE electrolytic enrichment method that spreads tritium into the environment in some degree. We believe when considering the impact to the environmental, the differences in our approach of controlling the tritium has significant meanings.

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