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Electrolytic Enrichment of Tritium in Water Using SPE Film

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1. Introduction

Just after Voltaic cell was invented at the beginning of eighteenth century, the cell was applied to electrolysis in water and it was found that water is composed of hydrogen and oxygen. Since this discovery stimulated the scientific understanding on the behavior of ions in solution with atomic level, the electrolytic technology spreaded to the various fields such as refining of metals, metal plating, generation of alkaline substances and removal of trace toxic materials in water and soil. And this technology nowadays becomes an important field in electrochemistry.

Since tritium is generated at the stratosphere by the nuclear reaction of nitrogen and neutron and decays with radioactive half-life of 12.3 years releasing beta-ray, it always exists in a constant amount in nature. On the other hand, large amounts of tritium were produced by the nuclear bomb tests in the atmosphere until the early 1960s and it fell out all over the world, although the concentration of the fallout tritium is lowered to the background level because it passed for several decay times of half-life. Tritium is also generated from atomic power plants and atomic fuel reprocessing plants currently and tritium contaminated waste vapor is released to the air and the wasted water into seawater now in the world. Then the flow of the released waste has to be monitored to know the diffusion process in the environment and to keep the safety in mankind and ecosystem.

Liquid scintillation counting system is used to count the released electrons by the beta-decay. Lower limit of tritium concentration in a low background liquid scintillation counting system is around 0.4 Bq/L for counting time of 1000 minutes using 100 mL vial (Hagiwara et al., 2012). As tritium concentration in environment is 1 Bq/l or lower and especially lower than 0.5 Bq/L in seawater in Japan (Yamashita & Muranaka, 2011), it is difficult to measure the concentration even using such a low background liquid scintillation counting system. To solve the problem tritium concentration in sample water is enriched by

water electrolysis before counting. Since the tritium concentration in the enriched water exceeds the lower limit of the counting system, the concentration can be measured with the sufficient accuracy even for seawater.

Various methods are proposed to obtain the enrichment factor in the tritium electrolysis in sample water. Among the suggested methods a method using apparatus constant presented by Kakiuchi, M. et al. (Kakiuchi et al., 1991) is noteworthy because the constant is not so fluctuated comparing with a separation factor (Inoue & Miyamoto, 1987). Details are described in the next paragraph.

Tritium enrichment apparatus by electrolysis is roughly classified into two categories. One is the method using alkaline electrolyte and another is that using solid polymer electrolytic film (SPE film). Electrolysis using SPE film was established firstly by Saito, M. et al. (Saito et al., 1996) and a large current apparatus was developed commercially (Saito, 1996). SPE film is used as a medium to carry hydrogen ions from anode electrode to cathode one in electrolytic cell instead of OH^- in alkaline electrolysis. Since this method has merits that alkalizing and neutralizing process of electrolytic solution is not necessary and there is no limit for electrolytic enrichment factor, this method is used in many groups recently.

Since it is important to know the tritium concentration in seawater at the area in Aomori prefecture, Japan because tritium contaminated waste is released into coastal seawater after the reprocessing is opened at Rokkasho, Aomori, Japan. We therefore tried the experiment of electrolytic enrichment in water with a handmade electrolytic device used SPE film from the mid age of 1990's (Muranaka & Honda, 1996).

Although Saito, M. et al. made an electrolytic apparatus which can release hydrogen and oxygen gas separately to remove the accident of the explosion by the mixing of the two gases, we designed an electrolytic device which can be put into the sample water cell as in the alkaline electrolysis (Muranaka & Honda, 1996; Muranaka et al., 1997). Method and apparatus for electrolytic enrichment are described precisely in section three and characteristics of the designed devices are described in the section four.

Tritium concentrations in seawater samples collected along the Pacific coast in Aomori prefecture, Japan were below 0.3 Bq/L except for the case in which the sample collection and the release of tritium contaminated wastewater into coastal sea from the atomic fuel reprocessing plant are matched in time (Muranaka & Shima, 2011). Tritium concentrations in land water in Aomori prefecture are around 0.5 Bq/L, very low comparing with those collected twenty years ago in the same locations. These results are described in section five in detail.

2. Electrolytic enrichment of tritium in water

2.1. Principle of electrolytic enrichment

The basic formulas for electrolysis are shown in equation (1)~ (3). (1) is the reaction in anode electrode, (2) is that in cathode one and (3) shows the whole reaction for electrolysis.

Tritium, deuterium and light hydrogen exist in water as THO, DHO and H₂O, respectively. It is confirmed experimentally that H₂O is easily electrolyzed than THO and DHO. Tritium and deuterium in water thus are enriched after the continued electrolysis. Schematic diagram of electrolytic enrichment using SPE film is depicted in Fig.1. In anode electrode sample water is decomposed into oxygen and hydrogen ion and the generated H⁺ ion passes through the SPE film. This H⁺ ion is combined to the electron arrived at cathode electrode through the external electric circuit and is released as hydrogen gas.

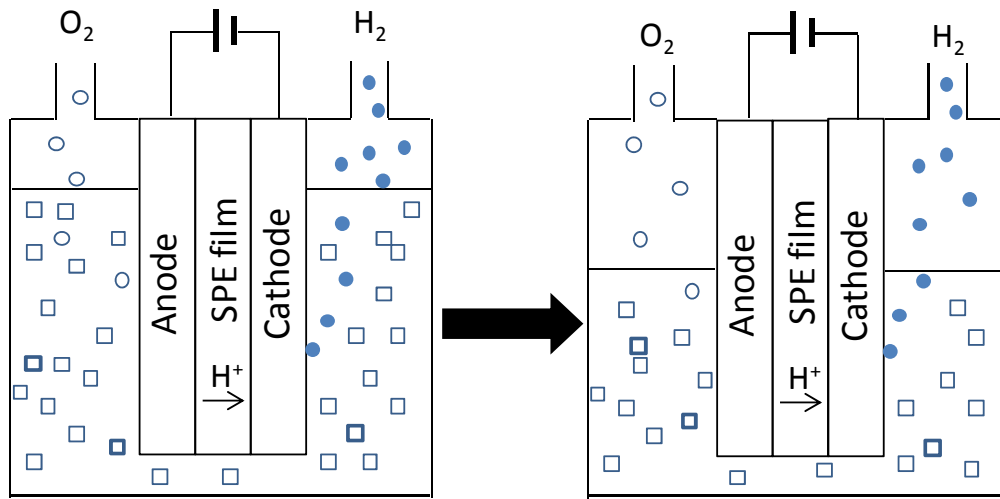


Figure 1. Electrolytic enrichment of tritium in water.

Opened squares in the electrolytic cell represent H₂O and those with comparatively thick border show THO or DHO. Opened and filled circles mean oxygen gas and hydrogen gas, respectively. Electrolysis proceeds from left hand figure to right hand one, that is, the number of THO or DHO molecules are not so reduced although those of H₂O molecules are gradually decreased in the process of electrolysis.

2.2. Determination of tritium enrichment factor

2.2.1. A method using tritium recovery factor

Tritium recovery factor which is defined by (4) is used to determine tritium enrichment factor in electrolytic enrichment.

$$R = (T_f \cdot V_f) / (T_i \cdot V_i) \quad (4)$$

Where T_i and T_f represent tritium concentration before and after the electrolytic enrichment, and V_i and V_f indicate the volume of sample water before and after the enrichment. Tritium concentration before enrichment can be represented by (5) which is transformed from (4).

$$T_i = T_f / ((V_i / V_f)R) \quad (5)$$

Since V_i/V_f in (5) means the reduction factor in sample volume, tritium concentration before enrichment can be obtained dividing tritium concentration after the enrichment by the product of volume reduction factor and tritium recovery factor in the electrolytic enrichment. This product therefore means the tritium enrichment factor. In the constant volume reduction factor, tritium concentration before the enrichment can be deduced from only the tritium concentration after the enrichment if tritium recovery factor in the enrichment is provided using standard sample water. To obtain correct volume reduction factor volume of sample water before and after the enrichment must be measured precisely. The volume or the weight of sample water after the enrichment is especially necessary to be measured correctly to obtain the tritium concentration in sample water accurately, because the volume after the enrichment is lower than that before enrichment and the error rate becomes larger.

2.2.2. A method using apparatus constant

An apparatus constant is defined by (6)(Kakiuchi et al.,1991).

$$k = \ln(T_f / T_i) / \ln(D_f / D_i) \quad (6)$$

Tritium concentration can be given by (7) transforming the expression of (6).

$$T_i = T_f / (D_f / D_i)^k \quad (7)$$

Deuterium concentration before and after enrichment and apparatus constant are contained instead of the product of volume reduction factor and tritium recovery factor as the tritium enrichment factor in the expression of (7). If apparatus constant for electrolytic cell is determined, tritium concentration can be deduced from tritium concentration after the enrichment and deuterium concentration before and after the enrichment.

The relation between tritium recovery factor R and tritium separation factor β is shown in (8) (Inoue & Miyamoto, 1987). In (9) the relation between apparatus constant and tritium separation factor β and deuterium separation factor α is represented(Kakiuchi et al.,1991).

$$R = (V_f / V_i)^{1/\beta} \quad (8)$$

$$k = \alpha(\beta-1) / \beta(\alpha-1) \quad (9)$$

Tritium separation factor β is known to be varied by some experimental factors such as electrode materials, surface condition of the electrode, current density in electrolytic enrichment, temperature in the water and so on (Satake & Takeuchi, 1987; Inoue & Nam, 1994). But it is confirmed that apparatus constant is not so vary, although α and β are varied by the run condition of the repeated electrolysis (Kakiuchi et al.,1991).

It is estimated that the variation of α and β is canceled in the apparatus constant represented in (9). Therefore the use of apparatus constant and deuterium concentration before and after the enrichment will be better than that of volume reduction factor and tritium recovery factor to obtain tritium enrichment factor correctly.

3. Method and apparatus for electrolytic enrichment

3.1. An electrolytic enrichment of tritium using alkaline electrolyte

In the conventional method for electrolytic enrichment of tritium a pair of metal electrode is set in an electrolytic cell and sodium peroxide (Na_2O_2) is added to the sample water in the cell to give it the electric conductivity. As the structure of this type of electrolytic cell is so simple that two or more cells can be connected in series and electrolytic enrichment in multiple cells is possible to be electrolyzed at the same time. Schematic diagram of two electrolytic cells in series is shown in Fig.2.

On the other hand this method has a disadvantage of a tedious process after the electrolysis that electrolytic material must be neutralized and the precipitation material has also to be removed from the solution. Another demerit of this method is that electrolytic enrichment factor is limited by the solubility of the electrolyte.

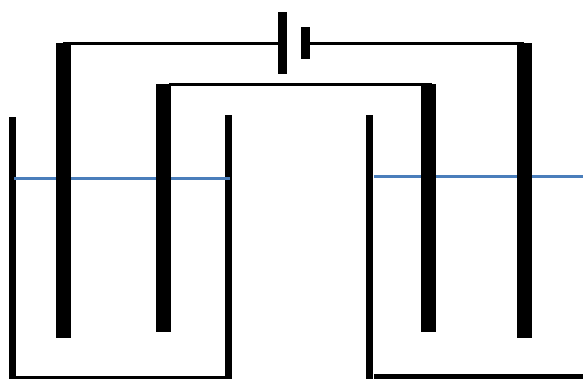


Figure 2. Electrolytic enrichment of tritium concentration in sample water connecting each cell in series.

3.2. An electrolytic enrichment of tritium using SPE film

3.2.1. SPE film

Water electrolysis using SPE film is started by G. E. in USA at 1970s applying fuel cell technology. The used SPE film is a kind of cation exchangeable membrane (NAFION[®] 117, Dupont).

This membrane is composed of carbon-fluorine backbone chains with many perfluoro side chains containing sulfonic acid groups (SO_3^-) and hydrogen plus ion can wade through the groups as depicted in Fig.3. The hydrogen ion reached to the cathode through the membrane film receives an electron from the external electric circuit and a pair of hydrogen atoms are connected to be hydrogen gas.

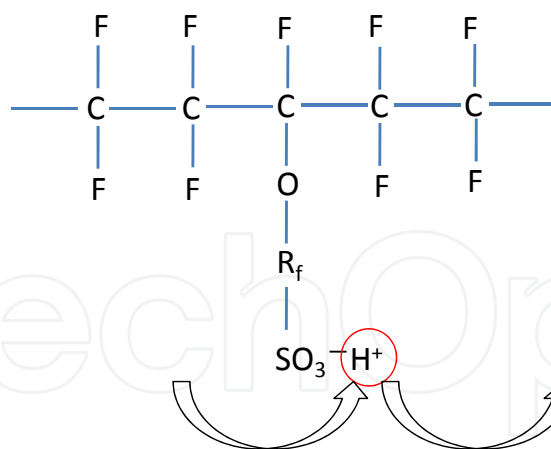


Figure 3. The structure of SPE film and the transfer of hydrogen ion from a sulfonic acid group to the next one.

In this method sample water can be enriched by electrolysis without adding any electrolyte to the water and then the tedious process after the electrolysis is not necessary and the enrichment factor is not limited by the solubility of the electrolyte. In addition to these merits electrolytic current can be increased removing generated gases quickly from the surface of both electrodes.

3.2.2. Electrolytic apparatus using SPE film

3.2.2.1. Oxygen-hydrogen separating apparatus

Oxygen- hydrogen separating apparatus using SPE film was originally devised by Saito et al. (Saito et al., 1996). Schematic diagram is shown in Fig.4.

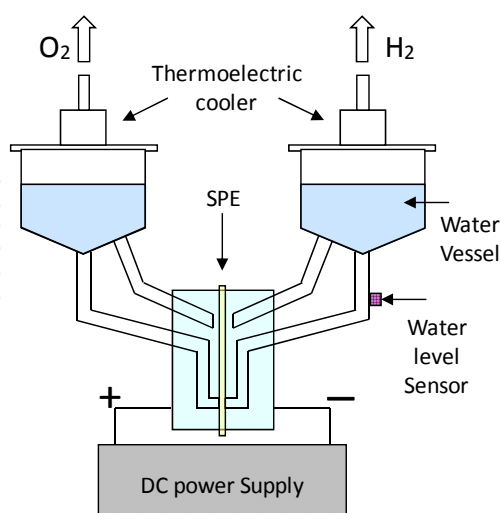


Figure 4. Schematic diagram of electrolytic cell devised by Saito et al..

In this type of electrolytic device SPE film is sandwiched by porous electrodes, water vessels being connected at the bottom are placed in both side of electrodes, oxygen and hydrogen

gases are released from each side of water vessel through the thermoelectric cooler to avoid the evaporation loss of water. Water level sensor is also provided not to exceed the lower limit of the water volume. This type of electrolyzer which can operate by a large electrolytic current of 50A was released commercially from Permelec Electrode LTD.

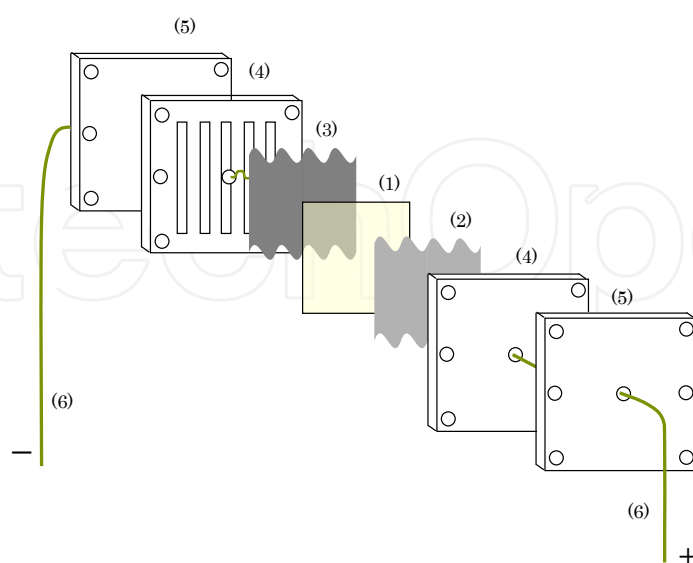
3.2.2.2. Oxygen-hydrogen non-separating apparatus

We designed an electrolytic device using SPE film like a conventional cell using alkaline electrolyte, because this type is simple in structure, can be connected in series and is easy to be cooled by a chiller.

1. An electrolytic device using corrugated electrodes

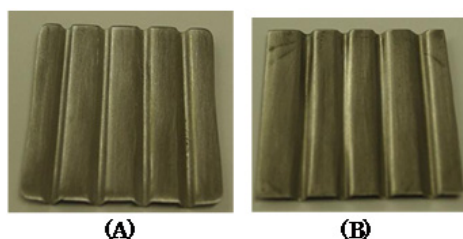
At the beginning an electrolytic cell having corrugated electrodes was designed. The composition of the device and the photograph of the electrode are represented in Fig.5 and in Fig.6, respectively. Generated oxygen and hydrogen gases are released from not in contact space between the electrode and SPE film in the vertical direction (Muranaka & Honda, 1996; Muranaka et al., 1997; Shima, 2007) .

The size of SPE film is 4.2cm square, used electrode is 4cm×4cm in size, 0.2mm in thickness and Teflon plate and acrylic plate are 6cm square. Slots in the Teflon plate can be grooved to fit the folded dents in the electrode. Acrylic plate placed in the outermost is used to keep the position of the each part including gold lead wire of 0.6mm in diameter tightening with stainless steel bolts. Anode electrode is made of platinum plate to avoid the dissolution during the electrolysis. The electrolytic cell has a capacity of 1.9L, is made of polypropylene, 28cm in height, 10cm in diameter at upper side and 8.5cm at the bottom. This electrolytic cell is set in the cooling water bath and is cooled at two degrees centigrade or lower in the bath.



(1)SPE film(NAFION®117), (2)corrugated anode (platinum plate), (3)corrugated cathode(nickel plate), (4)Teflon plate, (5)acrylic plate, (6)gold lead wire.

Figure 5. Schematic diagram of the initial type electrolyzer.



(A) and (B) represent an anode made of platinum plate and a cathode of nickel plate, respectively.

Figure 6. Photographs of the electrodes used for the initial type electrolyzer.

2. A newly designed electrolytic device using porous electrode

The drawback of the device using corrugated electrodes is that electrolysis is not carried out at not in contact area between the electrode and SPE film, and generated gas cannot be released smoothly at in the contact area. Although the lead wire contacts to the electrode with a spiral form to increase the contact area, electrolytic current could not be increased because of the heat loss by the electric current between the lead wire and the electrode not in contact to the wire directly. A new electrolytic device was designed to improve these faults. Schematic diagram of the electrolyzer is shown in Fig.7. (A) is the figure for the elements, (B) is the cross section and (C) is the assembly drawing of the electroplyzer (Shima & Muranaka, 2007b; Shima, 2007; Muranaka & Shima, 2008).

SPE film(1) in (A) and (B) is Nafion117. Anode (2) is made of porous titanium metal covering with rare metals and their oxides. Cathode (4) is made of porous stainless steel. Dimensionally stable electrode (DSE) manufactured by Permelec Electrode was used as the porous electrode. These electrodes asked were 4cm square and 2.6mm in thickness. Platinum mesh (3) was inserted between the SPE film and the anode DSE so that the cell can be easily dismantled without the detachment of the catalyst from the base metal electrode. The porous electrode (5) used to collect electrolytic current is made of gold, 4cm square and has many small holes of 1.0mm in diameter. These two plates allowed for homogenous current flow through SPE film and for release of electrolytic gases. Current lead wire is touched to the folded edges of the current collector to maintain the electric contact between the two elements. A spacer (6) was placed between the supports (7) to maintain constant separation between the elements of the electrolytic device. The spacer serves to restrict the thickness of the SPE film as it absorbs water from sample water and swells. These supports have many small holes of 1.5mm in diameter distributed coaxially to the holes of the current collectors to release the generated gases smoothly.

In Fig.8 electrolytic device positioned in the cell is shown (Shima & Muranaka, 2007b). Electrolytic device is placed in a container so that it could be tilted slightly in order to release oxygen gas generated beneath the anode electrode. Hydrogen gas released from the cathode electrode can therefore rise vertically without any obstacles. Generated oxygen and hydrogen gases are released in a mixed condition like an alkaline electrolysis. Although this method is felt to be dangerous at a glance, the burst timing of the bubbles containing hydrogen gas is different from each other and the released hydrogen is diffused into the air immediately. Since the released hydrogen gas mass from the bubble is therefore departed

from the explosion limit each other, it will be safe up to some electrolytic current in such a open system.

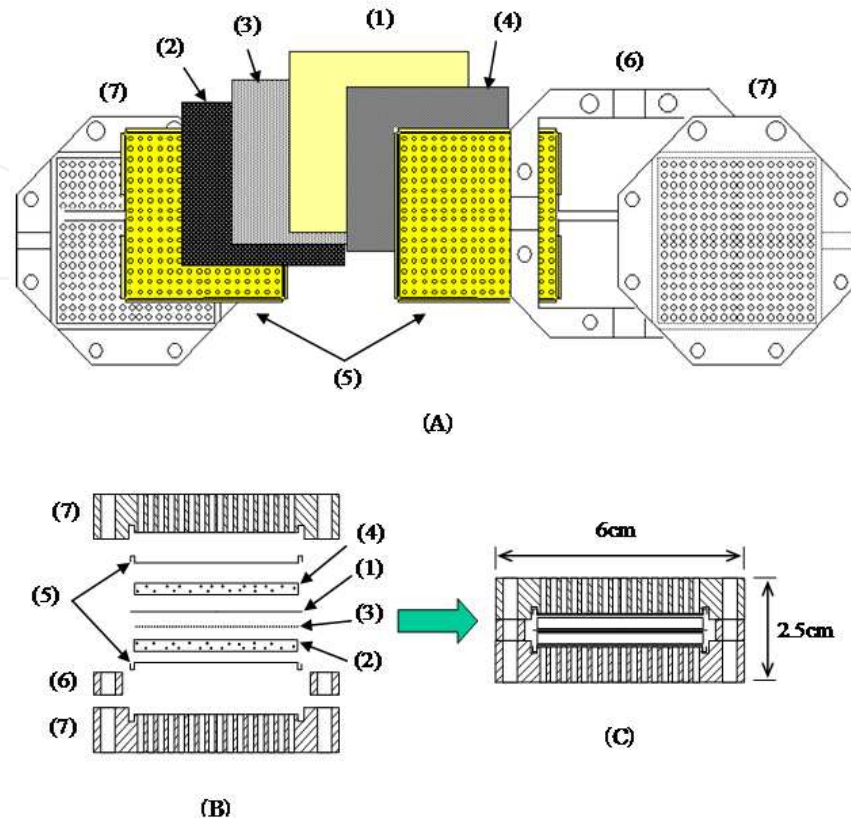


Figure 7. Schematic diagram of the electrolyzer.

(A) is the figure for the element, (B) is the cross section and (C) is the assembly drawing of the electrolyzer. (1) SPE film(Nafion 117), (2) porous anode DSE, (3) Pt mesh, (4) porous cathode DSE, (5) electrolytic current collectors, (6) spacer, and (7) support (Shima & Muranaka, 2007b; Shima, 2007; Muranaka & Shima, 2008). [(A) partly modified and (B) were reprinted with permission from Japan Radioisotope Association and the American Nuclear Society.]

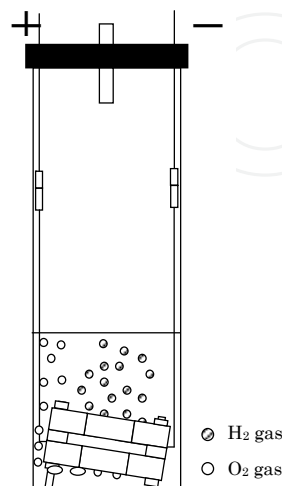
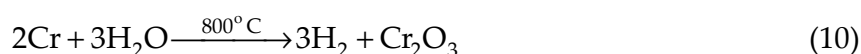


Figure 8. Schematic diagram of the electrolytic cell containing the newly designed electrolytic device (Shima & Muranaka, 2007b). [Reprinted with permission from JRA]

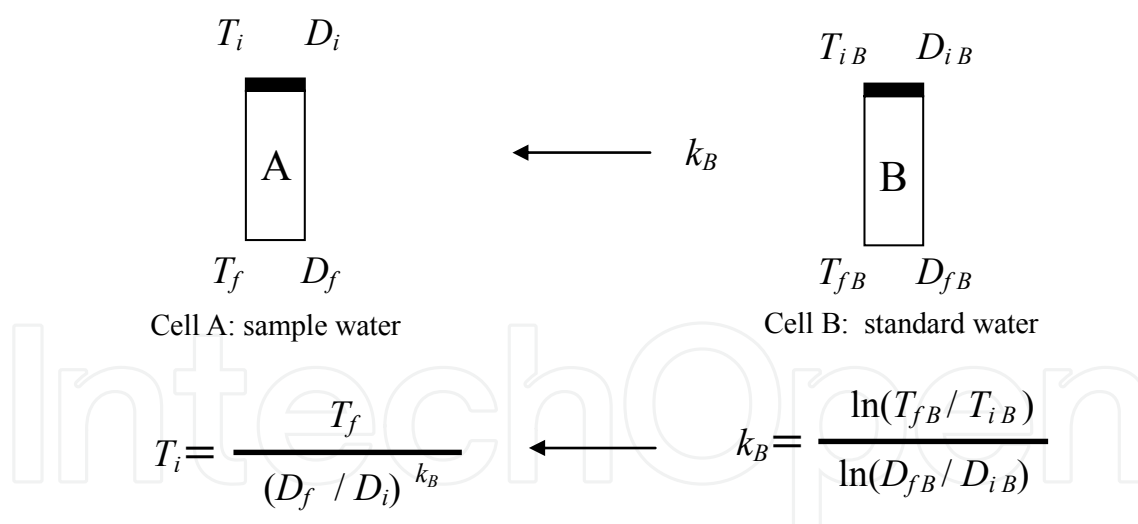
4. Characteristics of the electrolytic device

Tritium in water samples were measured by a low background liquid scintillation counting system (LB-II, Aloka). Enriched water of 40mL and a scintillator solution (Aquasol-2, Packard) of 60mL were mixed in Teflon vials. Tritium concentrations were estimated by beta ray counting, with each sample counted ten times over a period of 50 minutes for four cycles. Total counting time for each sample was therefore 2000 minutes. To prevent erroneous results due to electrostatic charges on the surface of sample vial, we removed the first three of the ten repeated counts and estimated tritium concentrations using the residual counting data. The hydrogen stable isotope ratio was measured by an isotope ratio mass spectrometer (Delta plus, Thermo Fisher Scientific) connected to a pretreatment device (H/Device, Thermo Fisher Scientific). Water droplets (1.2μL) were converted to hydrogen gas in this device according to the chemical reaction (10)(Sato et al., 2005).



4.1. Characteristics of the electrolytic device using corrugated electrodes

Water samples were enriched using the same tritium concentrations in two cells in series to demonstrate the apparatus constant derived from cell B could be used to estimate the tritium concentration in cell A. The flow chart is represented in Fig.9.



T_i : Tritium concentration in sample water before enrichment
 T_f : Tritium concentration in sample water after enrichment
 D_i : Deuterium concentration in sample water before enrichment
 D_f : Deuterium concentration in sample water after enrichment
 T_{iB} : Tritium concentration in standard water before enrichment
 T_{fB} : Tritium concentration in standard water after enrichment
 D_{iB} : Deuterium concentration in standard water before enrichment
 D_{fB} : Deuterium concentration in standard water after enrichment

Figure 9. Flow chart of calculating tritium concentration in cell A connected to standard cell B in series using an apparatus constant in the neighbor cell of B.

A tritium contained solution was prepared each time with a concentration of about 8 Bq/L, inputted to both cells of A and B and electrolyzed from the initial weight of 300g to the final one of 60g with the electrolytic current of 3A which corresponds to the current density of about 0.2A/cm² in the device. Experimental results are presented in Table 1 (Muranaka et al., 2005). Tritium concentrations in four prepared samples were initially measured to be in the range from 7.56 to 8.12 Bq/L. In Table 1 T_{iB} and D_{iB} in cell B are considered to be equal to T_i and D_i in cell A, respectively because the same prepared solution is divided into two cells of A and B. But T_{fB} and D_{fB} in cell B are considered not to be equal to T_f and D_f in cell A, respectively because the electrolytic condition is not same during the long time electrolytic run although these two cells are connected in series. Apparatus constants calculated from data in Table 1 are shown in Table 2. Tritium and deuterium concentrations after the enrichment in cell A are shown in Table 3. And in Table 4 calculated tritium concentrations using the apparatus constant derived each run in Table 2 and those using an averaged apparatus constant are represented as "Estimated (1)" and as "Estimated (2)", respectively together with the directly measured values. In the case using each apparatus constant differences between the directly measured and estimated results are in the range of 0.7 to 2.5%, with the average difference of 1.5%. Conversely, if we use the averaged apparatus constant of 1.070 from Table 2, the difference increased to the range of 0.7 to 7.5% with the average difference being 3.8%. From this result it is confirmed that the apparatus constant obtained from each electrolytic run is preferable to the averaged apparatus constant of the four results in this experiment.

No.	T_{iB} [Bq/L]	D_{iB} [%]	T_{fB} [Bq/L]	D_{fB} [%]
1	7.56	0.0147	26.61	0.0468
2	7.69	0.0148	27.30	0.0459
3	8.09	0.0147	25.75	0.0442
4	8.12	0.0148	25.81	0.0459

Table 1. Tritium and deuterium concentration in electrolytic enrichment test. Suffix B means standard cell B corresponding to Fig.9. T_{iB} and D_{iB} in cell B are considered to be equals to T_i and D_i in cell A, respectively as explained in the text (Muranaka et al., 2005). [Reprinted with permission from ANS]

No.	T_{fB}/T_{iB}	D_{fB}/D_{iB}	Ratio (T_{fB}/T_{iB})/(D_{fB}/D_{iB})	Apparatus constant k_B
1	3.52	3.18	1.106	1.087
2	3.55	3.10	1.145	1.119
3	3.18	3.01	1.059	1.052
4	3.18	3.10	1.025	1.022
Average	3.36	3.10	1.083	1.070
$\pm \sigma$	± 0.21	± 0.07	± 0.05	± 0.04
C.V.[%]	6.3	2.3	4.9	3.9

Table 2. Enrichment ratios and derived apparatus constants (Muranaka et al., 2005). [Reprinted with permission from ANS]

No.	T_r [Bq/L]	D_r [%]
1	26.00	0.0469
2	27.77	0.0459
3	26.55	0.0450
4	26.20	0.0469

Table 3. Tritium and deuterium concentrations after the enrichment in cell A.

No.	Direct value [Bq/L]	Estimated (1) [Bq/L]	Difference [%]	Estimated (2) [Bq/L]	Difference [%]
1	7.56	7.37	2.5	7.51	0.7
2	7.69	7.83	1.8	8.27	7.5
3	8.09	8.18	1.1	8.02	0.9
4	8.12	8.06	0.7	7.63	6.0
		Average	1.5	Average	3.8

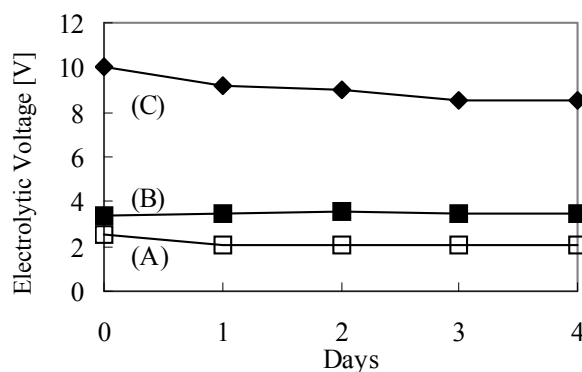
Table 4. Difference between directly measured and the estimated tritium concentrations in the experiment (Muranaka et al., 2005). [Reprinted with permission from ANS]

4.2. Characteristics of a newly designed electrolytic device used porous electrodes

Electrolytic voltages for three kinds of electrolytic devices described in the paragraph three are shown in Fig.10 (Muranaka & Shima, 2008). (A) is the variation of an electrolytic voltage for a commercially available apparatus, (B) represents that for a newly designed device and (C) is that for the conventional device using corrugated electrodes. Electrolytic current is 6A for (A) and (B) which corresponds to the current density of about 0.3A/cm² and 0.4A/cm² for the device of (A) and (B), respectively and the current is 3A (0.2A/cm²) for (C). Although the structure in the devices of (A) and (B) is different, the electrolytic voltage in both devices are lower than that in the device of (C). Decrease of the voltage will therefore depend on the used materials for the electrodes. The electrolytic time will be shortened because electrolytic current can be increased with small electric power in both devices of (A) and (B). The voltage for the device (B) is somewhat higher than that for (A). One of the origin is the platinum mesh inserted between the anode and SPE film for the device (B) to separate them after the electrolysis easily.

Tritium recovery factors which are defined by the formula of (4) are represented for the device of (A) and (B) in Table 5 (Muranaka & Shima, 2008). Electrolytic current is 6A for all experiments. Electrolytic enrichment was repeated to study the stability of both cells. R3, R5 and R10 in the table mean that the volume reduction factors are three, five and ten, respectively. Coefficient of variation (C.V.) is in the range of 0.5 to 2.5% and the difference in the stability for both devices is not so large. Tritium recovery factor of five times in the device (B) is larger than that in the device (A). This will be caused from the temperature in

the sample solution. Sample water in the device (A) is cooled by air cooling, on the other hand that in the device (B) is cooled by water bath.



(A) is a commercially available apparatus (TRIPURE XZ027, PERMELEC ELECTRODE LTD), (B) is the newly designed electrolytic device, and (C) is a conventional enriching device equipping with corrugated metal electrodes. The electrolytic current is 6A for (A) and (B) which corresponds to the current density of about 0.3A/cm² and 0.4A/cm², respectively, and the current is 3A (0.2A/cm²) for (C) (Shima & Muranaka, 2007b, Muranaka & Shima, 2008). [Reprinted with permission from JRA and ANS]

Figure 10. Electrolytic voltages during electrolysis.

No.	(A)	(B)		
	R5	R3	R5	R10
1	0.658	0.902	0.860	0.774
2	0.681	0.910	0.831	0.782
3	0.676	0.913	0.810	0.783
4	0.676	0.910	0.843	0.768
Average	0.673±0.010	0.909±0.005	0.836±0.021	0.777±0.007
C.V.(%)	1.5	0.6	2.5	0.9

Table 5. Comparison of tritium recovery factors obtained using (A) the commercially available apparatus, and (B) the newly designed electrolyzer. R3, R5 and R10 mean that volume reduction factor in the electrolysis are 3, 5 and 10, respectively. C.V. means the coefficient of variation (Muranaka & Shima, 2008). [Reprinted with permission from ANS]

Apparatus constant was studied by Kakiuchi, M. (Kakiuchi, 1999) and tritium and deuterium separation factor were measured by Momoshima, N. et al. (Momoshima, et al., 2005) on the characteristics of the commercially available device.

4.3. Two-stage electrolysis

Electrolytic enrichment is possible by the electrolytic current up to 50A for commercially available apparatus. This ability leads to the shortening of the enrichment time. On the other hand, tritium recovery factor for the newly designed device is larger than that for the large current electrolytic apparatus and the decomposition of the device is easier in the designed device. Therefore we adopted a two-stage electrolysis using the large current electrolytic apparatus in the first stage and the designed device is used in the second stage (Shima & Muranaka, 2007a). In Fig.11 the flow chart is represented for this electrolytic method.

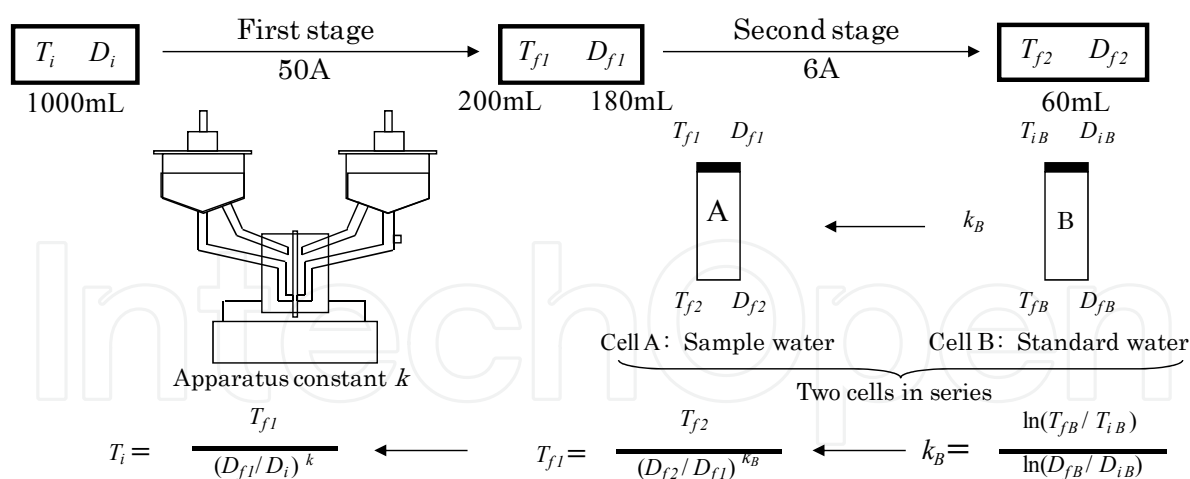


Figure 11. A flow chart of the two-stage electrolytic enrichment. T and D stand for tritium and deuterium concentration, respectively. Suffixes 1 and 2 indicate the stage of the enrichment, while suffixes i and f mean before and after enrichment, respectively. Suffix B indicates cell B which contains standard water.

Comparison of tritium recovery factors between one- and two-stage electrolysis is shown in Table 6. In the two-stage electrolysis sample water was enriched from 1000mL to 200mL by the commercially available apparatus and from 180mL to 60mL by the designed device as depicted in Fig.11. The volume reduction factor is 5 times in the first stage, three times in the second and the total volume reduction factor is therefore fifteen times. On the other hand, as sample water is enriched in the commercially available apparatus only from 900mL to 150mL by the electrolytic current of 50A and after that it is enriched to 60mL by the current of 20A, the total electrolytic reduction factor is same to the two-stage electrolysis mentioned before.

From Table 6 tritium recovery factor using such two-stage electrolysis is somewhat larger than that using one-stage enrichment. This is due to the higher tritium recovery factor of the second stage electrolysis using designed device showed in Table 5. Since this designed device is easy to decompose, it can be possible to reduce the tritium memory in the previous electrolysis exchanging SPE film in the designed device with a new one after finishing one run. As two-stage electrolysis combined both merits of the electrolyzers is useful, this system was adopted in the electrolytic enrichment of seawater described in the next section.

No.	one-stage enrichment	two-stage enrichment
1	0.583	0.659
2	0.593	0.649
3	0.602	0.662
Average	0.593 ± 0.010	0.657 ± 0.007

Table 6. Comparison of tritium recovery factors between one- and two-stage electrolysis.

5. Tritium concentration of land water and coastal seawater collected in Aomori prefecture, Japan

In 1985 the governor in Aomori prefecture, Japan accepted to construct an atomic fuel reprocessing facility at Rokkasho village in this prefecture. This fact motivated us to investigate tritium background concentration in environmental water in this area because tritium would be released to environment after the plant is completed. Low background liquid scintillation counting system was introduced in 1988 in our laboratory and the study began to start.

5.1. Tritium concentration in land water

5.1.1. Tritium concentration in land water twenty years ago

Tritium concentration in precipitation from 1990 to 1993 was measured at that time without pretreatment of electrolytic enrichment. Sampled water of 40mL was mixed to the scintillation liquid of 60mL (Aquasol2, Packard) in a Teflon vial of 100mL and the beta ray released from the sample solution was counted by the liquid scintillation counter (LB II, Aroka). Counting for fifty minutes was repeated four times for one vial and proceeded to the next vial. After all the placed vials on the conveyor belt were finished to count, these counting were repeated for seven cycles. Therefore total counting time for a vial is 1400 minutes. The calculation of tritium concentration was depended on the document issued by Science and Technology Agency at that time (Science and Technology Agency, Japan, 1977).

The concentration error corresponding with statistic error of 1σ is about $\pm 0.3[\text{Bq/L}]$. The detection limit is represented by (11) (Hagiwara et al., 2012).

$$A = (100 / E) \times (1000 / V) \times (K / 2) \times [K / T_s + ((K / T_s)^2 + 4N_b (1 / T_s + 1 / T_b))^{0.5}] \quad (11)$$

Where A means the detection limit with the unit of [Bq/L], K shows the width of the standard deviation (K equals three is used usually), T_s is the measuring time for sample water with the unit of second, T_b is that for background water with the same unit and N_b means the counting efficiency for background sample with the unit of cps.

Sampling was conducted at Hachinohe Institute of Technology, Japan. Precipitation was collected once a day after the precipitation.

The results were represented in Fig.12 to show the variation throughout the year (Muranaka & Honda, 1997). The detection limit was estimated about $0.6[\text{Bq/L}]$ using (11) for the counting condition and the tritium concentration below this value is therefore unreliable.

From the results it was confirmed that tritium concentrations are higher in the season from April to June than those in the period from August to September. This will be explained as follows. The moisture containing somewhat higher tritium concentration is mainly carried from the continent across the Sea of Japan in this season. On the other hand, precipitations in the period from August to September mainly carried by Typhoon or Tropical cyclone generated at Pacific Ocean where tritium concentration is lower.

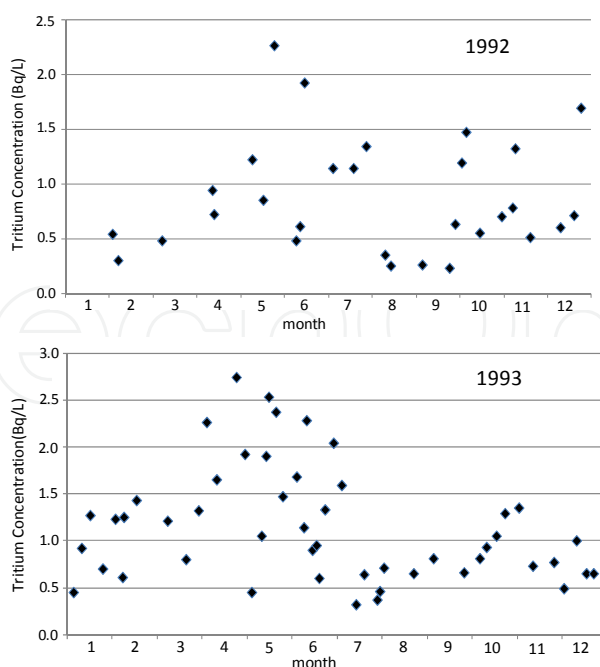
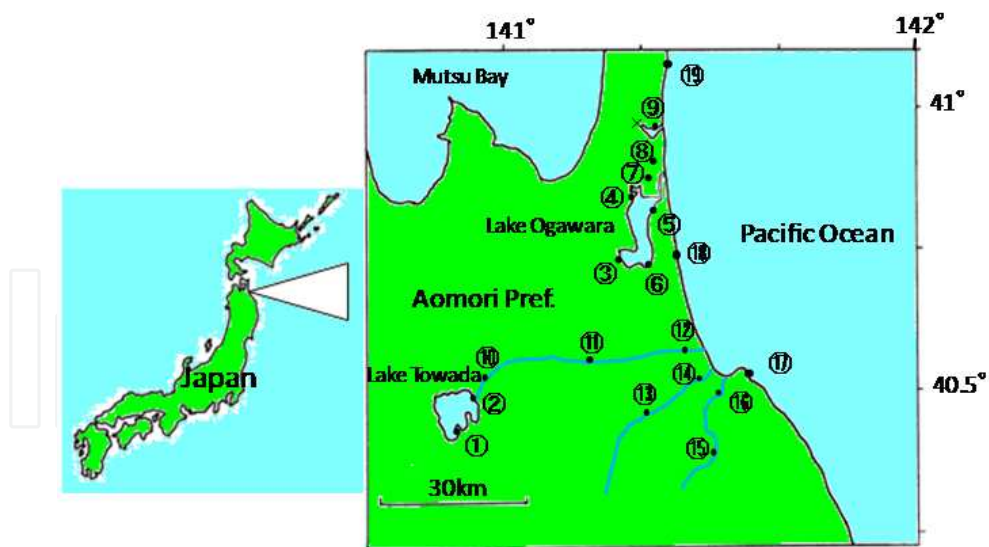


Figure 12. Tritium concentration in the precipitation collected at Hachinohe institute of technology in 1992 and 1993.

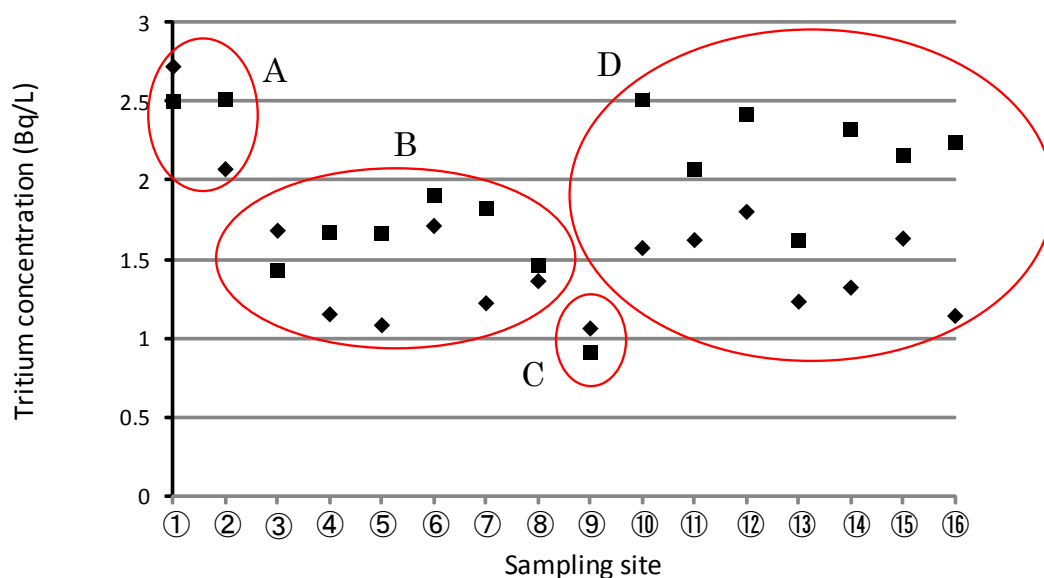
Sampling locations of lakes, marshes and rivers in Aomori prefecture, Japan are depicted in Fig.13. Water volume of 1L was sampled at each site once a year on a continued sunny period in autumn.



①Lake Towada, Yasumiya, ②Lake Towada, nenokuchi, ③Lake Ogawara, touhoku, ④Lake Ogawara, Rokkasho, ⑤Lake Ogawara, Yawata, ⑥Lake Ogawara, Misawa, ⑦Tamogi marsh, ⑧Ichiyanagi Marsh, ⑨Obuchi marsh, ⑩Oirase river, Ishigedo, ⑪Oirase river, Miyuki bridge, ⑫Oirase river, Koun bridge, ⑬Mabechi river, Hukuda bridge, ⑭Mabechi river, Uruichi, ⑮Niida river, Simamori, ⑯Niida river, Ishidearai. ⑰Shirahama beach in Hachinohe city, ⑱Misawa fishing port and ⑲Tomari beach in Rokkasho village. Water samples were not collected in these three points of ⑰~⑲ twenty years ago. Seawater in these sites was collected since 2006 when sample water is able to be enriched by electrolysis. The cross symbol indicates the nuclear reprocessing plant.

Figure 13. Sampling locations of environmental water in Aomori prefecture, Japan

Tritium concentrations are represented in Fig.14 (Muranaka & Honda, 1997). They could be classified into four divisions. A shows the tritium concentration in Lake Towada. Since the groundwater which contains fallout tritium wells up from the bottom in Lake Towada, tritium concentration will be higher than other divisions. B is the division from Lake Ogawara which is a brackish lake. The tritium concentration is lower due to the mixing entering river water and inflow of seawater. C is the water collected at Obuchi marsh which is also brackish. But the mixing amount of seawater is so large that tritium concentration will become lower. Since river water in the division D is the mixed water of groundwater and precipitation, the tritium concentration is lower than the groundwater only like in Lake Towada. But the tritium concentration in D is higher than those in water sampled from brackish lakes.



Numbers in horizontal axis indicate sampling sites in the same way denoted in Fig.13. The notation of \blacklozenge and \blacksquare mean tritium concentrations in the sample collected in 1992 and 1993, respectively.

Figure 14. Tritium concentration in environmental water collected in 1992 and 1993 at Aomori area, Japan.

5.1.2. Recent tritium concentration in land water

Recent tritium concentration in land water has decreased gradually due to the lowering of the influence by the fallout tritium generated until the early 1960s. Land water samples were collected in 2010 at the several points same to those sampled twenty years ago. The volume of sample water is reduced from 800mL to 200mL by the electrolytic current of 50A and from 200mL to 80mL by 20A using the commercially available apparatus only with the volume reduction factor of ten times because tritium concentration is not so lower like seawater. The volume reduction factor is ten times corresponds to the tritium enriched factor of about 7.2 times. The results are presented in Fig.15 with the same divisions to Fig.14. Tritium concentration is in the range from 0.4Bq/L to 0.55Bq/L except for the sample collected at Obuchi marsh. Tritium concentration is decreased comparing with those

measured about twenty years ago. It is pointed out that tritium concentration in the sample collected at Lake Towada decreased and it becomes closer to that sampled in Lake Ogawara recently.

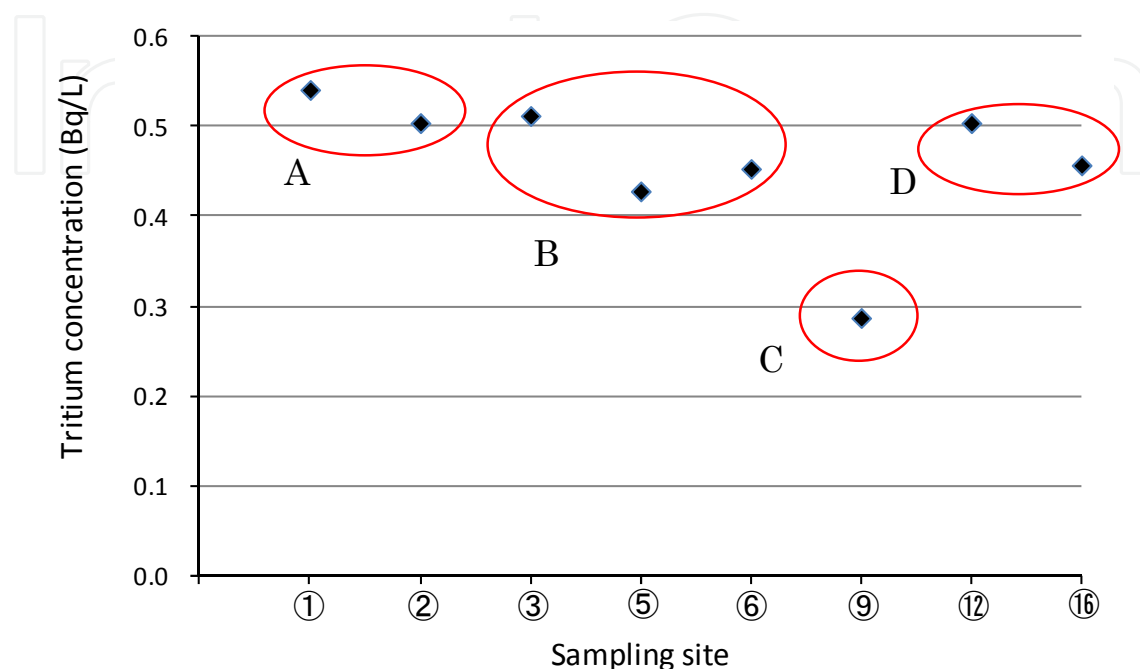
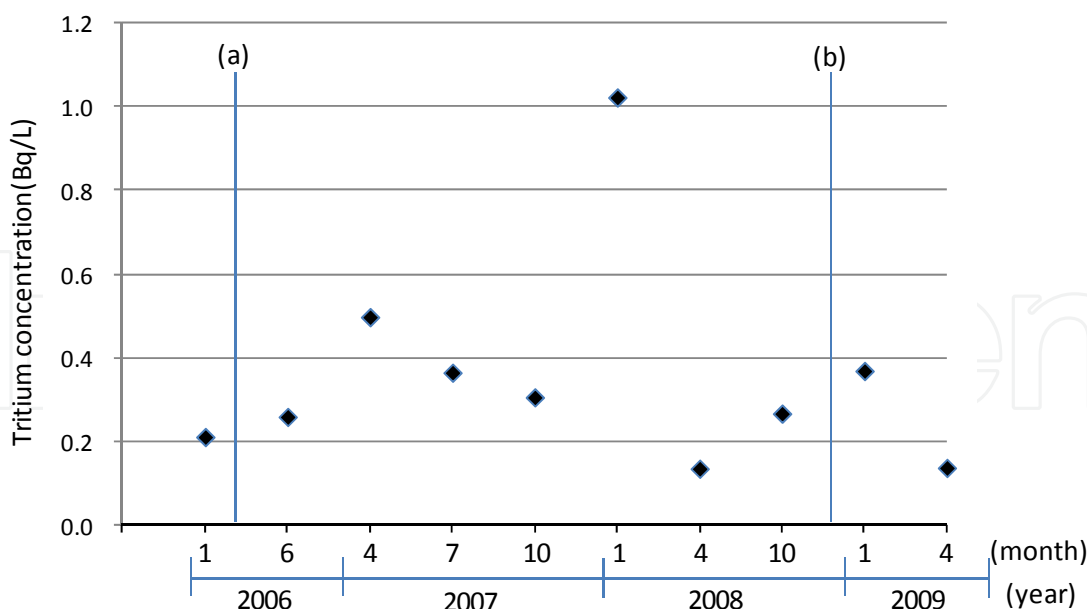


Figure 15. Tritium concentration in environmental water collected in 2010 at Aomori area. Numbers in the horizontal axis are same as those in Fig.13.

5.2. Tritium concentration in coastal seawater

Sampling points were selected along the coastal beach of the Pacific Ocean in Aomori prefecture including two southern sites, a northern site and a nearby site from the plant which is noted by the cross symbol in Fig.13. These sampling sites are indicated as the sites of ⑰~⑲ and ⑨. Samples were collected two or three times once a year. After sampled water was distilled under reduced pressure to remove contained salts, it was enriched by the two-stage electrolysis described in the section four.

Tritium concentration for the samples collected from Shirahama beach are shown in Fig.16 (Muranaka & Shima, 2011). Shirahama beach locates fifty five kilometers far from the nuclear reprocessing plant in the southern direction. (a) and (b) in Fig.16 indicate beginning (March, 2006) and the stop time (December, 2008) of the active test in the plant, respectively. Tritium concentration is less than 0.4 Bq/L outside of the period for the active test. But tritium concentrations are sometimes increased during the test. It was confirmed that the most prominent increase in tritium concentration observed on January 2008 is due to the tritium-contaminated waste water released from the plant (Muranaka & Shima, 2011). These temporary increase were observed at other three sampling sites.



(a) and (b) in the figure represent beginning (March, 2006) and the stop time (December, 2008) of the active test in the plant, respectively.

Figure 16. Tritium concentration in seawater collected at Shirahama beach in Hachinohe, Aomori, Japan (Muranaka & Shima, 2011). [Reprinted with permission from ANS]

6. Conclusion

Electrolytic enrichment using SPE film is an indispensable technology to study tritium concentration in environment nowadays. These devices are generally classified into two types. One is an oxygen-hydrogen separating apparatus and another is oxygen-hydrogen non-separating type. The former is commercially available and is useful to electrolyze a sample quickly with large electrolytic current. On the other hand the latter device also has some merits. It has higher recovery factor than the former device when the electrolytic cell is cooled by a chilly water bath and can prevent a memory effect from the previous run by exchanging SPE film with a new one. The reduced weight by electrolysis in the cell is able to measure by an electrolytic balance precisely. This last merit is especially useful in the case when the electrolytic volume after the enrichment is little due to the large volume reduction factor or the sample volume is originally little like water sample contained in plant. Since each electrolytic device has its own merit, two-stage electrolysis will be one of a practical method for the sample which has lower tritium concentration such as seawater. Among described analysis in environmental water samples in Aomori area coastal seawater was enriched by the two-stage electrolysis and it was confirmed that the tritium-contaminated waste water released from atomic fuel reprocessing plant at Rokkasho impacted to the tritium concentration in coastal seawater more than fifty kilometer far from the plant. Oxygen hydrogen non-separating electrolyzer has a potential to be used connecting in series to enrich tritium concentrations of several samples at once like a conventional alkaline method.

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