

**Effect of Tritium and of Radioactive Caesium Released
from the Accident of Fukushima Daiichi Nuclear Power
Plants on the Environment and the Construction Method
of Evaluation of Tritium Internal Exposure by Applying
Hydrogen Isotope Exchange Reaction**

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ABSTRACT

When tritium (T) in precipitation was produced by the interaction between ^{14}N (or ^{16}O) and ^1_0n , the specific activity of T in environment is $0.5\sim 1.0\text{Bq/kg}$ in Niigata. On the other hand, T is also produced by nuclear bomb test. When atmospheric nuclear-bomb test were performed (1960s), the maximum value of T was over 200Bq/kg in Niigata city. After that, the specific activity of T continuously decreased and attained the environmental level ($0.5\sim 1.0\text{Bq/kg}$). However, after the accident of Fukushima Daiichi Nuclear Power Plants, the specific activity of T in precipitation was increased in Niigata city. There are two processes of T production in a nuclear reactor. In this study, precipitation in Niigata city was collected monthly, and the evaluation of the specific activity of T was performed. In addition, we also collected the precipitation hourly (short precipitation) and spring waters of several mountains in and around Fukushima prefecture. Furthermore, radioactive caesium and T in some lake sediments in Fukushima and Niigata was investigated.

T also causes a hydrogen isotope exchange reaction (T-for-H exchange reaction), and can be divided into exchangeable organically bound tritium (OBT) and non-exchangeable OBT. Exchangeable OBT acts as Free Water Tritium (FWT) in the body, and the dose coefficient of T in FWT is unity. On the other hand, the dose coefficient of T in non-exchangeable OBT is 2.3. At present, distinction of exchangeable OBT and non-exchangeable OBT are very vague. Thus, the study on exchangeable OBT and non-exchangeable OBT is more important. In this study, the reactivity of hydrogen isotope exchange reaction for Exchangeable OBT and non-exchangeable OBT was observed. Consequently, the evaluation of internal exposure of T was performed.

From the above-mentioned, the following matters can be found.

- (1) The tritium concentrations in the samples in March and April 2011 were twice or three times higher than in March and April in annual years. In other words, it is considered that the thus high level concentration of tritium attributes the accident of the Fukushima Daiichi Nuclear Power Plants on Niigata city.
- (2) All of the activities of T in spring-water sample are less than 1.0Bq/kg and similar to the level of the monthly precipitation in Niigata city.
- (3) The specific activity of T in spring-water was not increased 3.5 years after 3.5 years from the accident of Fukushima Nuclear Power Plants.
- (4) Transfer coefficient of T from FWT to non-exchangeable OBT is 0.000070.
- (5) When internal exposure of T is calculated by applying the transfer coefficient, the amount of increase in dose is only $1.3\times 10^{-13}\mu\text{Sv}$. The increased does not affect human body.

As the results, the method used in this work can quantitatively clarify the reactivity of the T-for-H exchange reaction, and can be useful to estimate the internal exposure of exchangeable and non-exchangeable OBT.

CHAPTER 1

Tritium Behavior in the Precipitation from 2010 to 2014 in Niigata city

1.1 Introduction

Tritium (T) is a radionuclide of hydrogen and emits β^- ray. It seems that T does not cause the external exposure but cause the internal exposure because the energy emitted is very low (maximum 18.6keV). T is naturally produced by the interaction between ^{14}N (or ^{16}O) and ^1_0n . When T in precipitation was produced by only the above-mentioned, the specific activity of T in environment is 0.5~1.0Bq/kg in Niigata. On the other hand, T is also produced by nuclear bomb test. When atmospheric nuclear-bomb test were performed (1960s), the maximum value of T was over 200Bq/kg in Niigata city. After that, the specific activity of T continuously decreased and attained the environmental level¹⁾ (0.5 ~ 1.0Bq/kg). However, after the accident of Fukushima Daiichi Nuclear Power Plants, the specific activity of T in precipitation was increased in Niigata city. There are two processes of T production in a nuclear reactor. One is from the ternary fission. The other is the reaction between the deuterium and a neutron. In this study, precipitation in Niigata city was collected monthly and the evaluation of the specific activity of T was performed. In addition, we also collected the precipitation hourly (short precipitation). In order

to research the behavior of T in environment, an atmospheric diffusion was considered at the same time. The behavior of the precipitation was referred to back trajectory²⁾ and monitoring information of environmental radioactivity³⁾. Furthermore, other ion (Na^+ , Mg^+ , K^+ , Ca^{2+} , Cl^- , NO_3^- or SO_4^{2-}) concentrations in precipitation were measured. Previously¹⁾, the behavior of T is similar to one of non-sea salt Ca^{2+} (nssCa^{2+}). Therefore, in monthly precipitation, the specific activity of T and concentration of nssCa^{2+} was researched. Thus, T in the precipitation was clearly determined and the influence of the accidents of Fukushima Daiichi Nuclear Power Plants on environment was clarified.

1.2 Experimental

1.2.1 Sampling

Water samples of monthly and short precipitations were collected. Fig.1.1 shows the sampling point, Niigata University (37.87°N, 138.94°E). The plastic sampler⁴⁾ having copper wire at the neck of the container was used for monthly collection of precipitation. This sampler is similar to infiltrated groundwater

because the precipitation was overflowed up to 90%. Short precipitation was collected in large plastic sampler on 15th May 2011 and 19th April 2011. These precipitations were collected hourly.

1.2.2 Analytical method

Each water sample thus obtained was distilled with sodium peroxide and potassium permanganate. Then the water sample thus distilled was enriched by SPE (Solid Polymer Electrolysis) electronic enrichment apparatus⁵⁾. The enriched water (30ml) was added scintillator (100ml) and was eliminated static electricity. After thus preparation, the sample was left in a darkroom at low temperature for a week, and the activity of T was measured by a liquid scintillation counter. On the other hand, each ion concentration in the sample was measured by ion chromatography or Atomic Absorption Spectrometry.

In addition, backward trajectory analysis was performed and monitoring information of environmental radioactivity level was referred. Based on these analyses, the behavior of T was revealed.

1.3 Results and discussion

1.3.1 Monthly precipitation

Fig.1.2 shows the specific activity of T for monthly precipitation. Comparing each specific activity of T in 2011 with that in other years, the activity in spring 2011 is clearly increased. In Niigata city, the specific activity of T was generally increased on spring due to spring peak²⁾. However, the specific activity of T on March or April 2011 was clearly high because T may be diffused from the accident site of Fukushima Daiichi Nuclear Power Plants.

Fig.1.3 shows the concentration of nssCa^{2+} for monthly precipitation. On March and April 2011, the concentration of nssCa^{2+} is similar to that (on March and April in annual level). In other words, the specific activity of T can be thought as a similar level in annual value. However, because the effect of the accident of Fukushima Daiichi Nuclear Power Plants happened, the specific activity of T increased.

1.3.2 Short precipitation

In our laboratory research, the specific activity of T in short

precipitation is generally 0.5Bq/kg in Niigata city. Figs.1.4 and 1.5 show hourly specific activities of T on 15th March 2011 and 19th April 2011, respectively. On 15th March 2014, all the specific activities of T were about 2Bq/kg and 11.6Bq/kg at 18:00. It clearly shows the effect of the accidents of Fukushima Daiichi Nuclear Power Plants on precipitation. Furthermore, the specific activity of T was still high level on 19th April 2011.

1.3.3 Backward trajectory analysis

The specific activity of T in precipitation was influenced by air mass. Generally speaking, the air mass from the continent shows high value of T. On the other hand, air mass from Pacific Ocean shows low value. Figs.1.6 and 1.7 show backward trajectories on 15th March 2011 and 19th April 2011, respectively. In this analytical condition, the altitude is 1000m and length of time of back trajectory is 12h.

The air mass came from Yangzi jiang on 15th March 2011 and each transfer of the air mass did not change during several hours. However, the specific activity of T was increased at 18:00 because the ground wind came from the direction of Fukushima Daiichi Nuclear Power Plants. In the case of 19th April 2011, the specific activity of T was increased because the air mass was

also from Fukushima Daiichi Nuclear Power Plants.

1.4 Conclusion

From the above the mentioned, the following five matters can be found. (1) The tritium concentrations in the samples in March and April 2011 were twice or three times higher than in March and April in annual years. In other words, it is considered that the thus high level concentration of tritium leads to the evaluation of the effect of the accident of the Fukushima Daiichi Nuclear Power Plants on Niigata city. (2) As to the sample, the concentration of the non-sea salt Ca^{2+} (nss Ca^{2+}) is similar to that in March and April in annual years. (3) For each short precipitation sample collected on March 15th, 2011, the tritium concentration of each sample collected during 14:00~17:00 was about 2Bq/kg, but in during 17:00~18:00 was about 12Bq/kg. (4) For each short precipitation sample collected on April 19th, 2011, the tritium concentration was about 6 Bq/kg. (5) The tritium level in precipitation after May was similar to annual level (0.5~1.0Bq/kg).

From the above-mentioned, as to the precipitation on March 15th and April 19th, 2011, adding the consideration of air mass and the direction of the wind, it was revealed that tritium

concentration varied with the direction of the wind and an altitude.

From these results, it is thought that the effect of the accident of Fukushima Daiichi Nuclear Power Plants on Niigata city is so small.

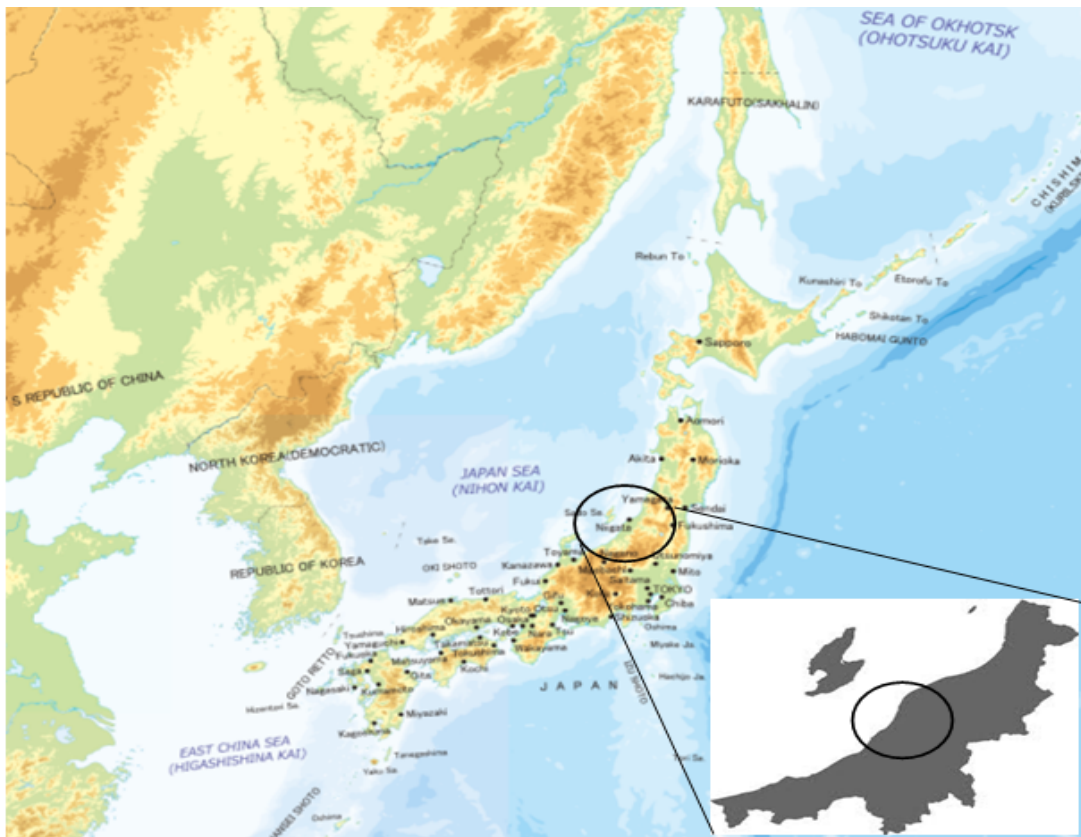


Fig.1.1 Sampling point of precipitation²⁾

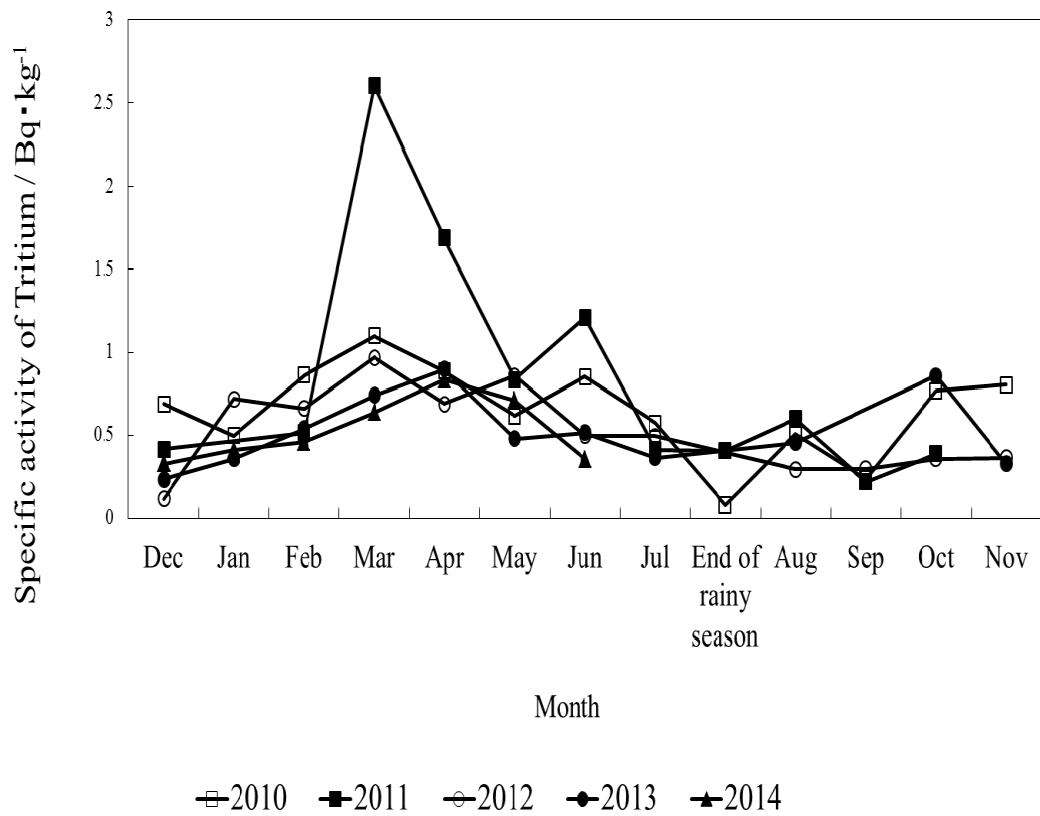


Fig.1.2 The comparison of each specific activity of tritium from 2010 to 2014 in Niigata city.

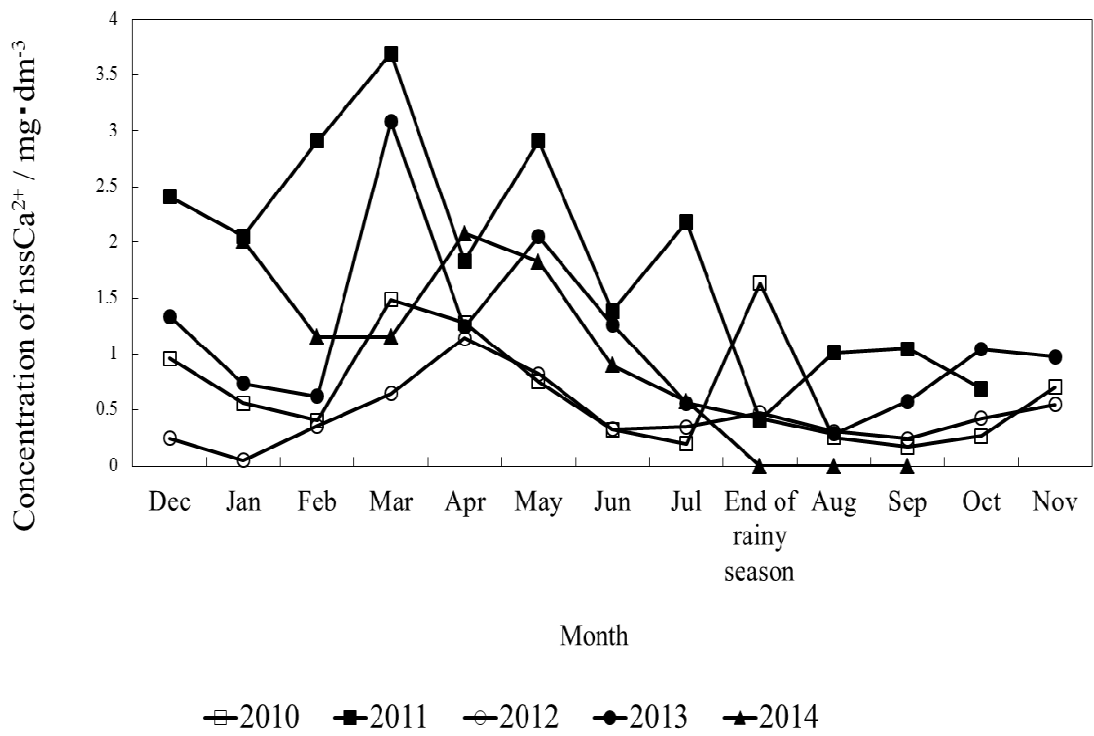


Fig.1.3 Concentration of nssCa²⁺
 from 2010 to 2014 in Niigata city.

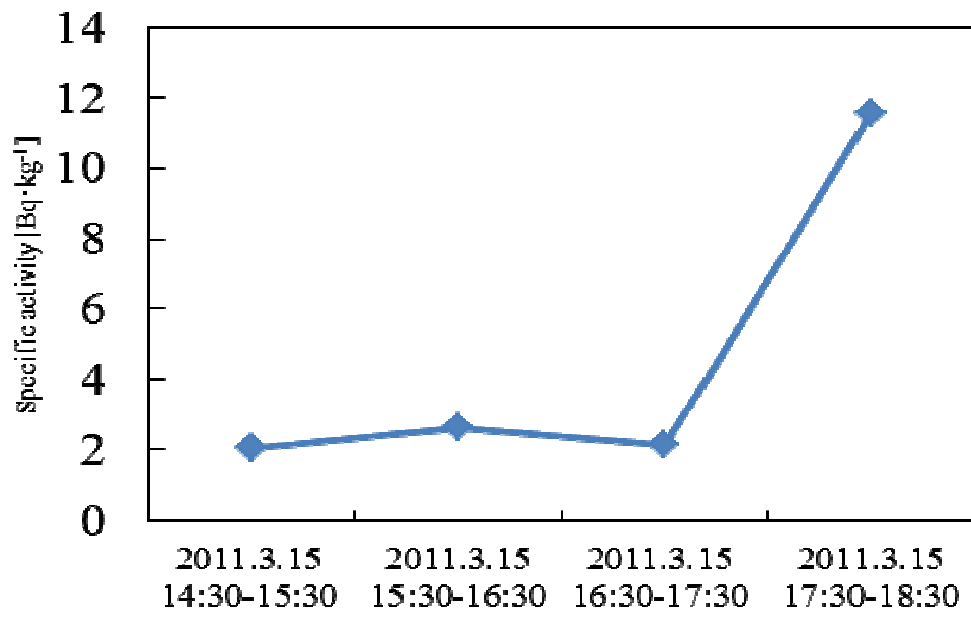


Fig.1.4 Specific activity of tritium in precipitation per hour on March 15th, 2011.

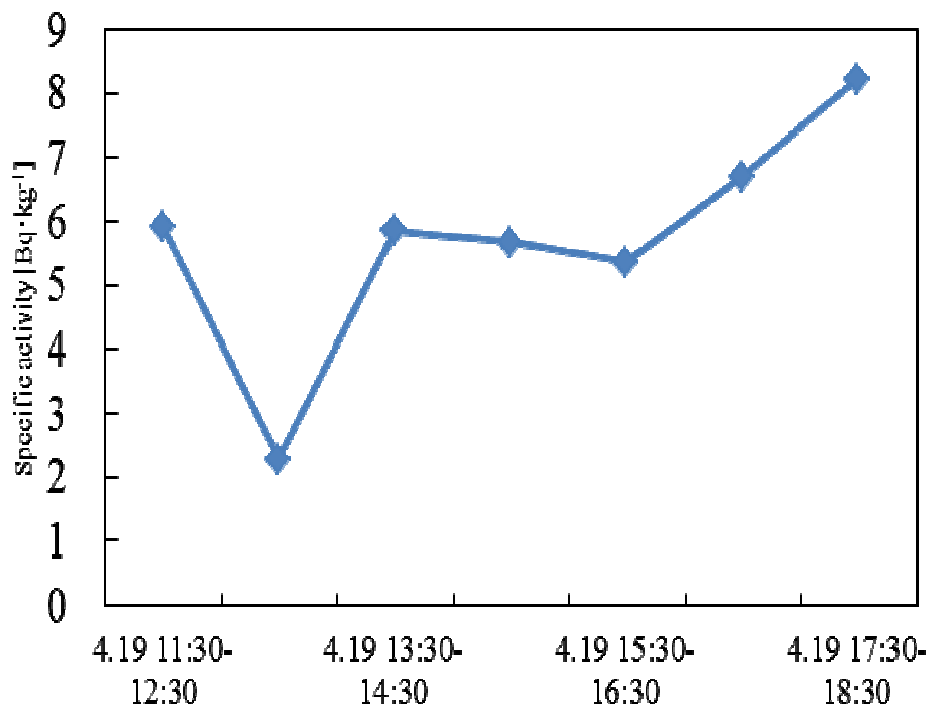


Fig.1.5 Specific activity of tritium in precipitation per hour on April 19th, 2011.

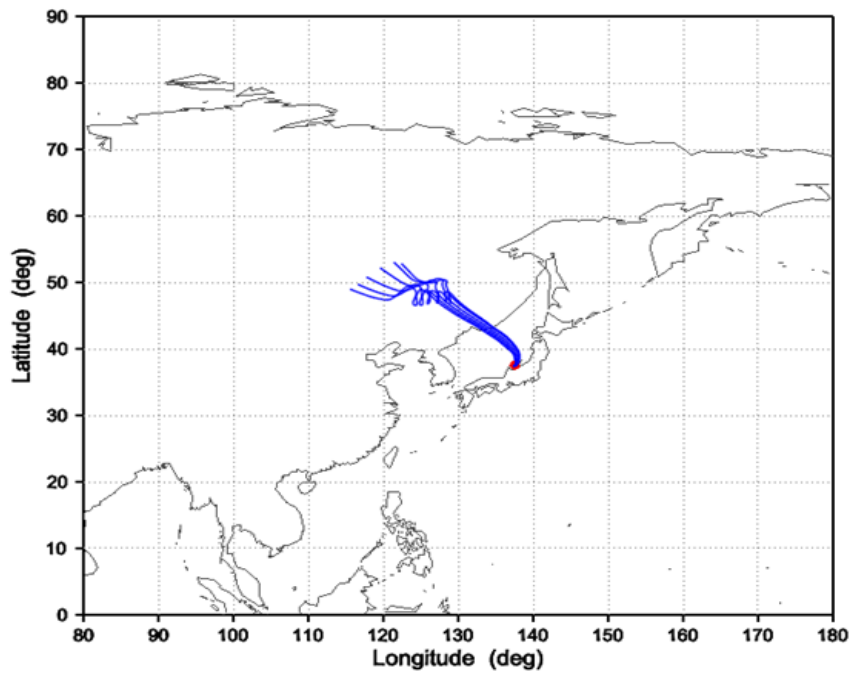


Fig.1.6 Backward trajectory of air mass based on 1 hour sample, March 15th 2011.

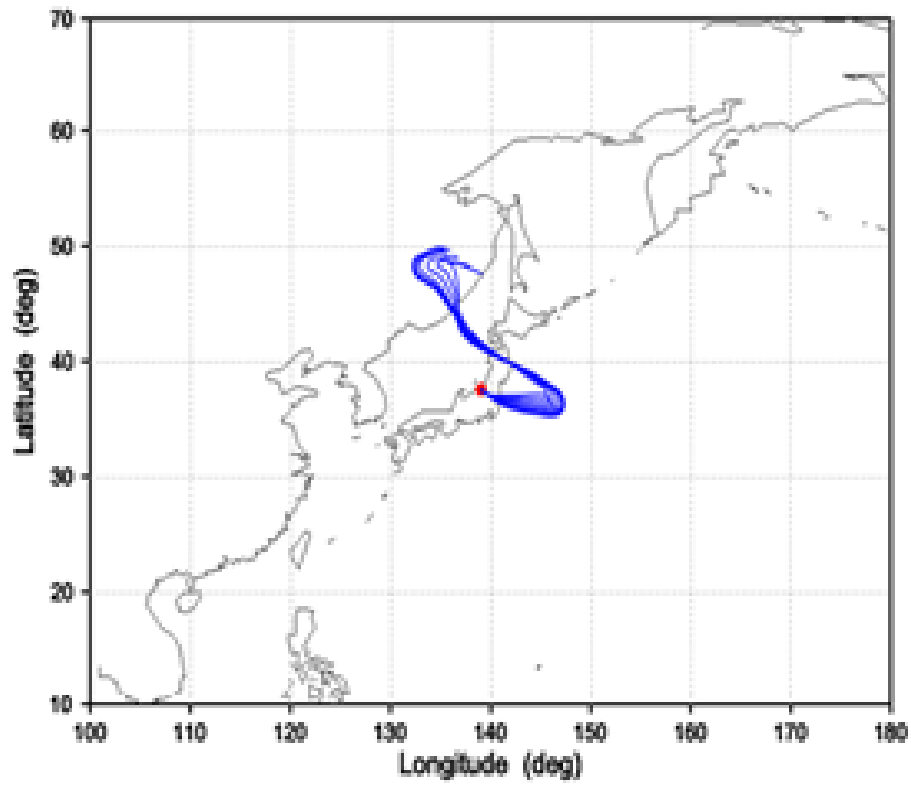


Fig.1.7 Backward trajectory of air mass based on 1 hour sample, April 19th 2011.

CHAPTER 2

Effect of Tritium in Spring-water around Fukushima Prefecture from the Accident

2.1 Introduction

In Former chapter, investigation of the influence of T was performed in Niigata city. But the specific activity of T must be investigated in Fukushima. In this chapter, each specific activity of T in and around Fukushima is investigated and discussed. Regarding to the spring water in mountains, the detention time of the specific activity of T in spring water is very long (over 2 years). Therefore, the influence of T may not appear immediately. In this study, sampling was carried out and, the sampling may be continuously performed.

2.2 Experimental

2.2.1 Sampling

Spring water was collected on August 2012 and 2013. The sampling points were in and around Fukushima prefecture (Bandaisan, Adatara, Abukuma, Zao).

2.2.2 Analytical method

Each water sample thus obtained was analyzed with the same methods shown in 1.2.2.

2.3 Results and discussion

Fig.2.1 shows each specific activity of T in spring water in the mountain. The background value of T in each sample water was not obtained before Fukushima Nuclear Power Plant accident. In this figure, the value of monthly precipitation on May 2013 in Niigata city was used as the value of background. All of the activities of T in sample water are less than 1.0Bq/kg and similar to the level of the monthly precipitation in Niigata city. Therefore, the T effect of the accident is not remained in the spring water. However, the research of spring water must be continued for several years because the detention time of the specific activity of T in the spring water in mountain is very long (about 2 years).

2.4 Conclusion

From the above mentioned, the following two matters can be found. (1) All of the activities of T in spring water sample are less than 1.0Bq/kg and similar to the level of the monthly precipitation in Niigata city. (2) Each specific activity of T in spring water was not increased even after the accident of Fukushima Nuclear Power Plants.

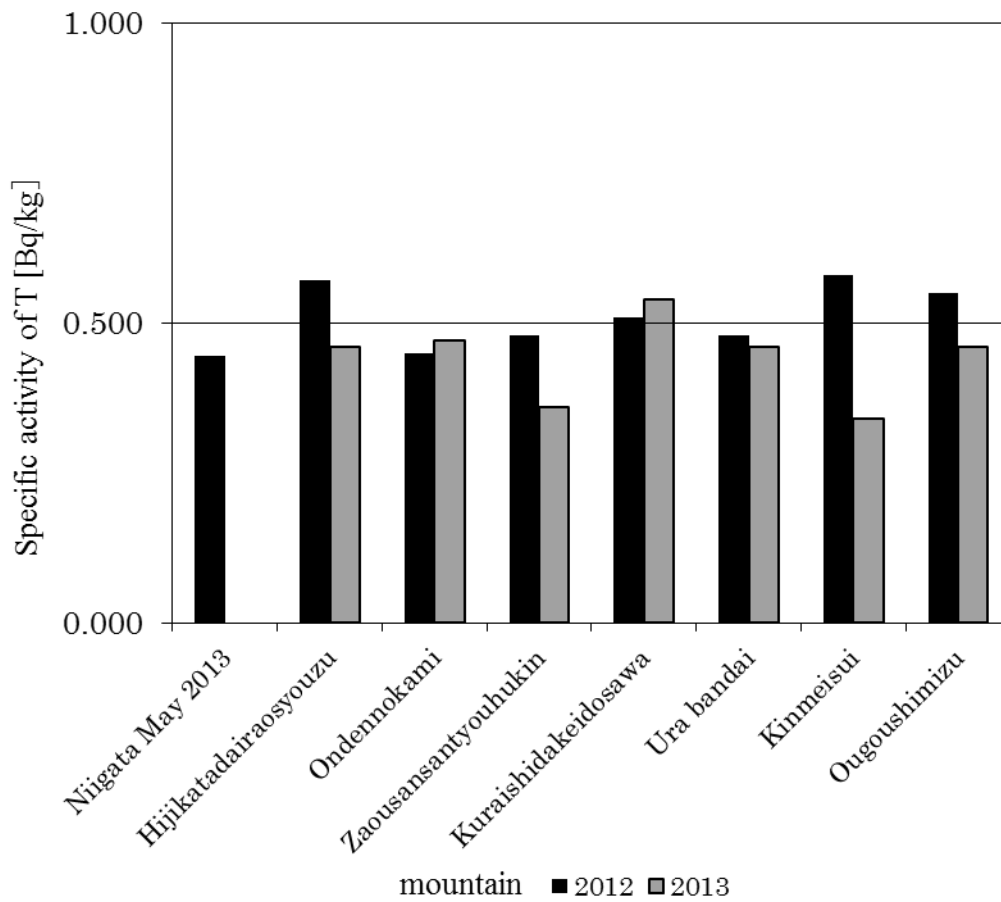


Fig.2.1 Specific activity of T in several mountains and the precipitation in Niigata city May 2013

CHAPTER 3

Research of the accident of Fukushima Daiichi Nuclear Power Plants on Lake in Fukushima and Niigata

3.1 Introduction

In this chapter, each lake water and each sediment was gathered on lakes in Fukushima and Niigata. Measurement radionuclides are T and radioactive caesium (^{134}Cs and ^{137}Cs). The production process of each radioactive caesium in nuclear power plants is shown Fig.3.1. ^{134}Cs (half time=2.04y) and ^{137}Cs (half time=30y) are produced from nuclear fission products. ^{137}Cs is produced by β^- decay from (mainly ^{137}I and ^{137}Xe). The half-life of β^- is very short (e.g. ^{137}Xe =3.9min). Therefore, ^{137}Cs is produced early if the nuclear fission reaction is performed. On the other hand, ^{134}Cs is produced by neutron irradiation from ^{133}Cs . When ^{134}Cs is produced by this method, it is important that the amount of ^{134}Cs depends on neutron irradiation time. In this accident of Fukushima Daiichi Nuclear Power Plant, the ratio of ^{134}Cs to ^{137}Cs is 1:1 on 15th March 2011. If the nuclear fission reaction dose not occurred after the accident, the activity of ^{134}Cs decreases with the half time. In this work, the radioactive caesium and T was investigated for two years. The relationship of radioactive caesium and T is also researched.

3.2 Experimental

The samples were collected in lakes in Fukushima and Niigata (Fig3.2 ~ Fig3.4). After the collection, these sampling water are distilled and enriched. Then the activity of tritium was measured by liquid scintillation counter (LSC). In addition, the radioactivity of ^{134}Cs and ^{137}Cs in these sediments were measured by germanium semiconductor detector.

3.3 Results and discussion

3.3.1 Specific activity of T

Fig.3.5 shows specific activities of T in the precipitation in Niigata city (May 2013) and the activity in the water in each lake. This figure indicates that deposition of T is easily affected by the topography and may accumulate at the place where convection does not occur. Especially, Lake Akimoto is surrounded by mountains, and it seems that the lake has a closed system. Therefore, specific activity of T at Lake Akimoto showed about twice as much as other lake water. In addition, Sakata lagoon in Niigata prefecture has a closed system too. From our previous research⁶⁾, it revealed that T specific activity in Niigata city was

increased by the accident. However, this research also showed that specific activity of T in Sakata lagoon was not so large. Accordingly, effect of the accident on Sakata lagoon could not be observed.

3.3.2 Specific activity of ^{134}Cs and ^{137}Cs

Specific activity of ^{134}Cs and ^{137}Cs in each lake sediment were shown in Figs 3.6 and 3.7. From the figures, it is found that the ratio of ^{134}Cs to ^{137}Cs was almost 1 : 2. Accordingly, it can be deduced that both ^{134}Cs and ^{137}Cs were emitted from the accident. As to the value of specific activity of each caesium in Lake Inawashiro (see Fig. 3.3), the activity at outflow place (Recreation Park at Lake Inawashiro) was higher than that at inflow place (Sakka lakeshore at Lake Inawashiro, and Tenjin beach at Lake Inawashiro). The other hand, the influence of the accident to Sakata lagoon in Niigata prefecture could not be found because radioactive caesium could not be observed. The relationship of radioactive caesiums and T is not clearly between sediment and water.

3.4 Conclusion

In order to reveal the effect of the accident of Fukushima Daiichi Nuclear Power Plants on lakes in Fukushima and Niigata, each lake water and sediment were collected and measured. From the results, the following conclusions are clarified.

(1) This research showed the effect of the accident on several lakes because the ratio of ^{134}Cs to ^{137}Cs was almost 1 : 2 after about 2 years. As to the lake specific activities of caesiums at outflow place were higher than that at inflow place.

(2) The measurement results show the T specific activity was similar to the value of precipitation recently collected at Niigata city. Therefore from the view of T, the effect of the nuclear accident may be no longer observed in Niigata city.

(3) It seems that if the lake does not circulate, T cannot move, and be accumulated there.

(4) The relationship of radioactive caesium and T is not clearly between the sediment and the water in each sampling point.

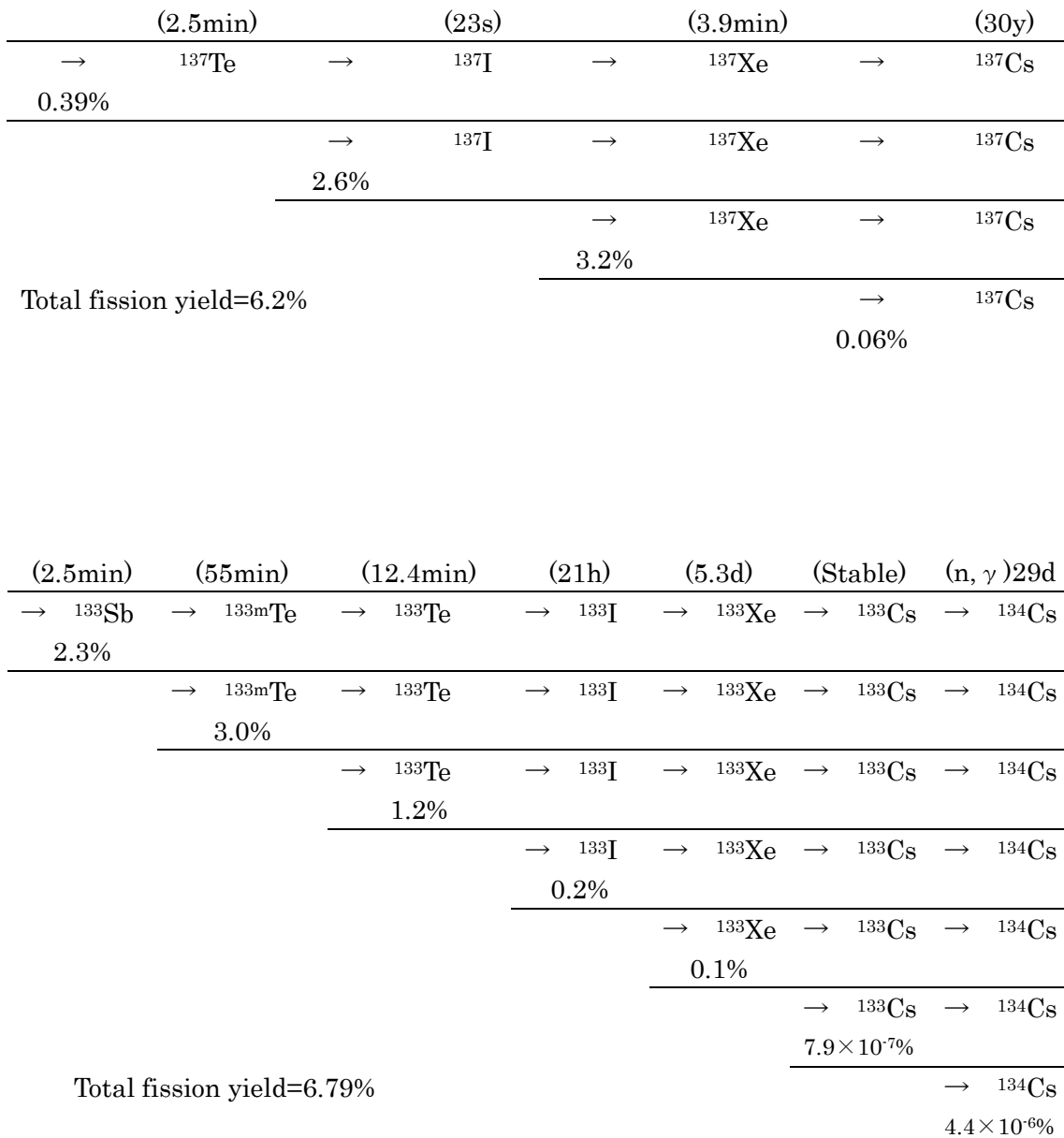


Fig.3.1 The production process of radioactive caesium in nuclear power plants

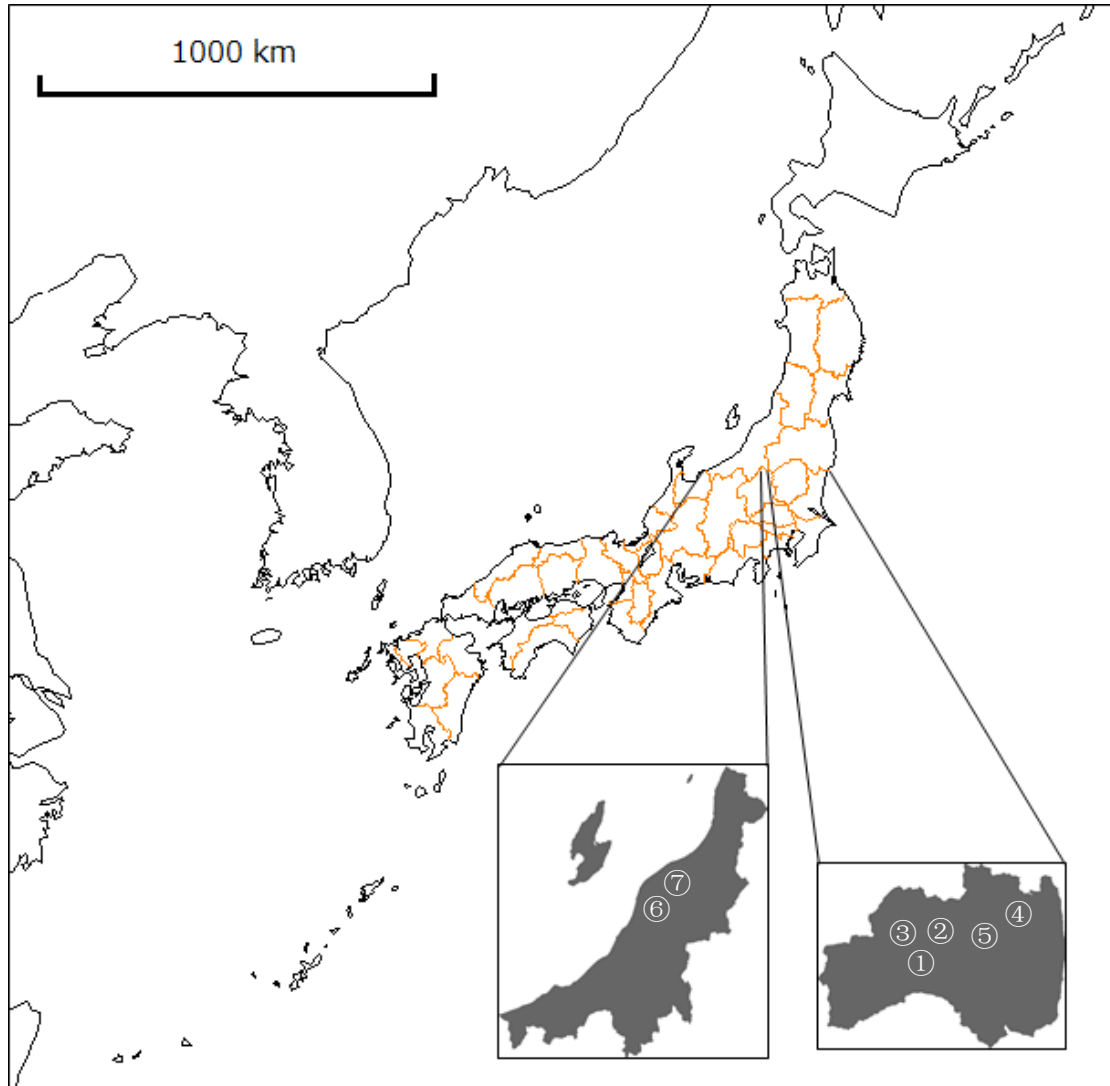
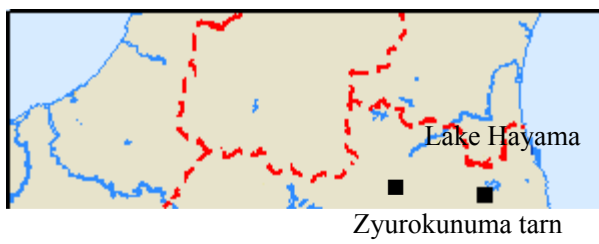


Fig.3.2 Locations of Niigata Prefecture and Fukushima Prefecture, and of Sampling points .

- ① Lake Inawashiro
- ② Lake Akimoto
- ③ Goshikinuma tarn
- ④ Lake Hayama
- ⑤ Zyurokunuma tarn
- ⑥ Sakata lagoon
- ⑦ Lake Toyanogata



Fukushima Daiichi
Nuclear Power Plants

20 km

Figs.3.3 The sampling points at Lake Inawashiro, Lake Akimoto, Goshikinuma tarn Zyurokunuma tarn and Lake Hayama in Fukushima Prefecture.



Fig.3.4 The sampling point at Lake Toyano and Sakata lagoon in Niigata Prefecture.

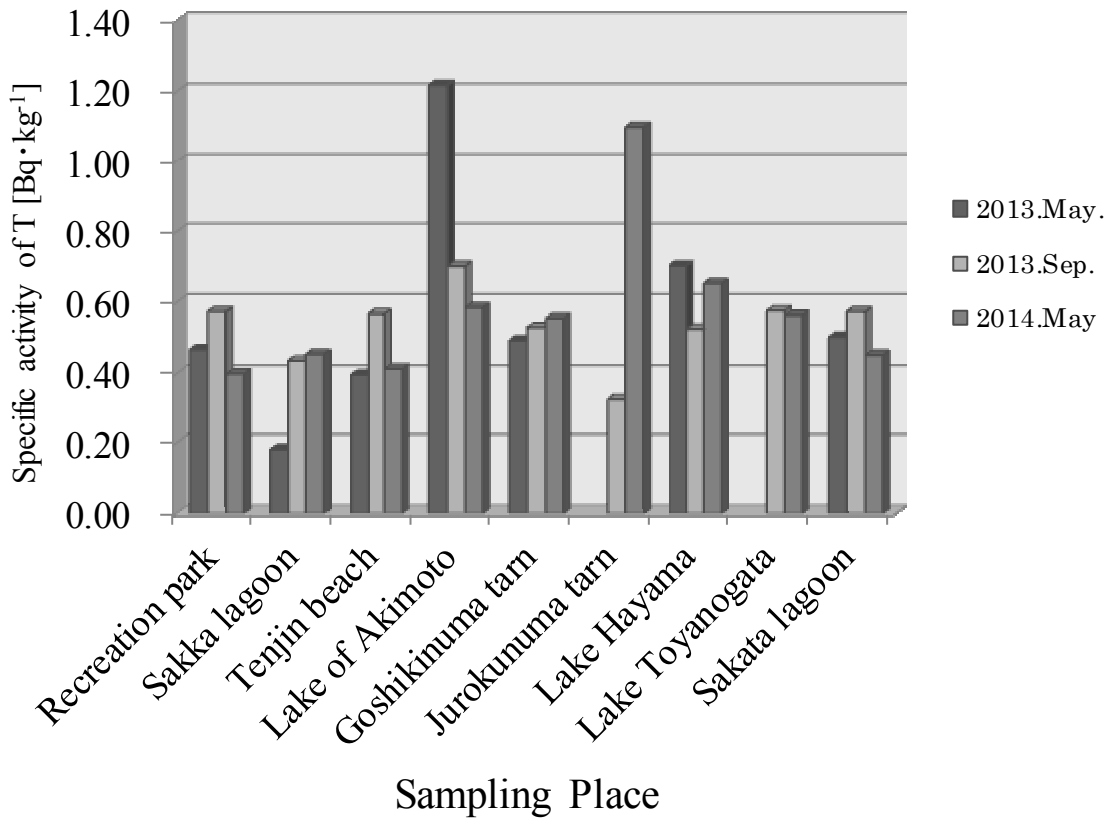


Fig.3.5 Specific activity of T in Fukushima and Niigata

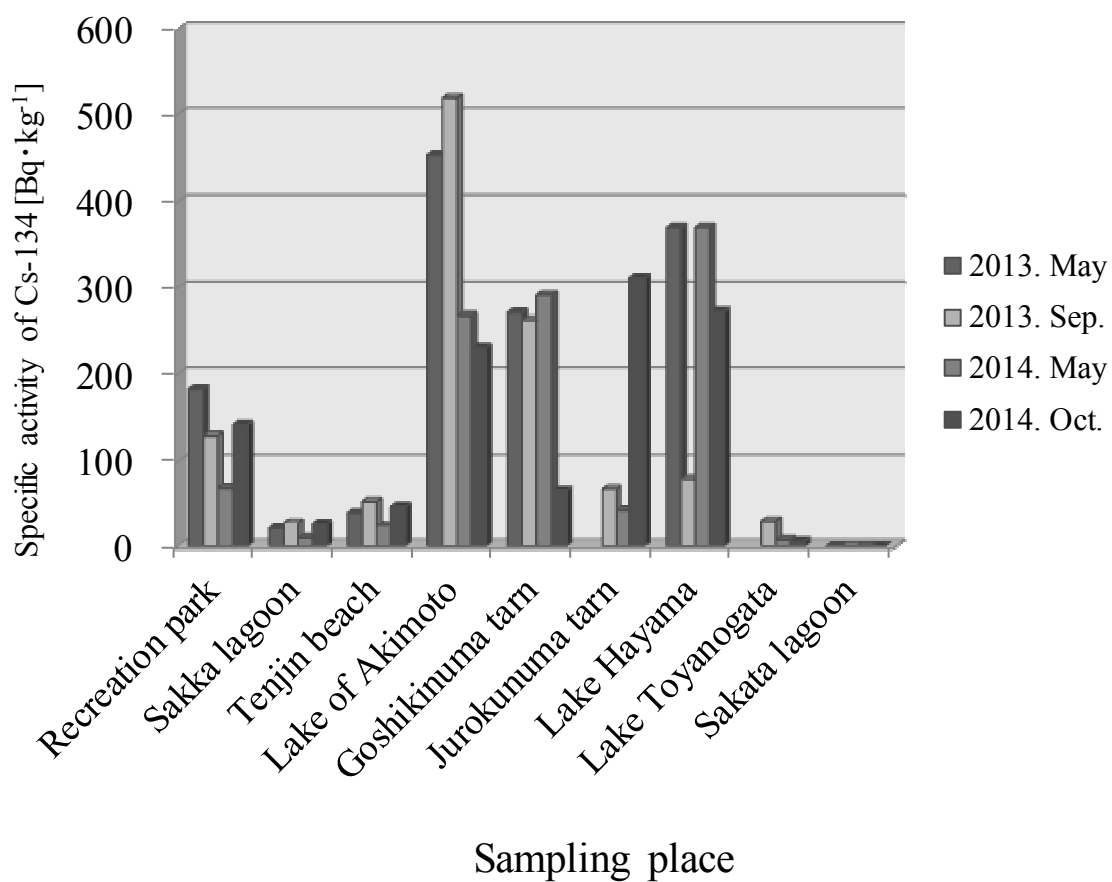


Fig.3.6 Specific activity of Cs-134 in Fukushima and Niigata

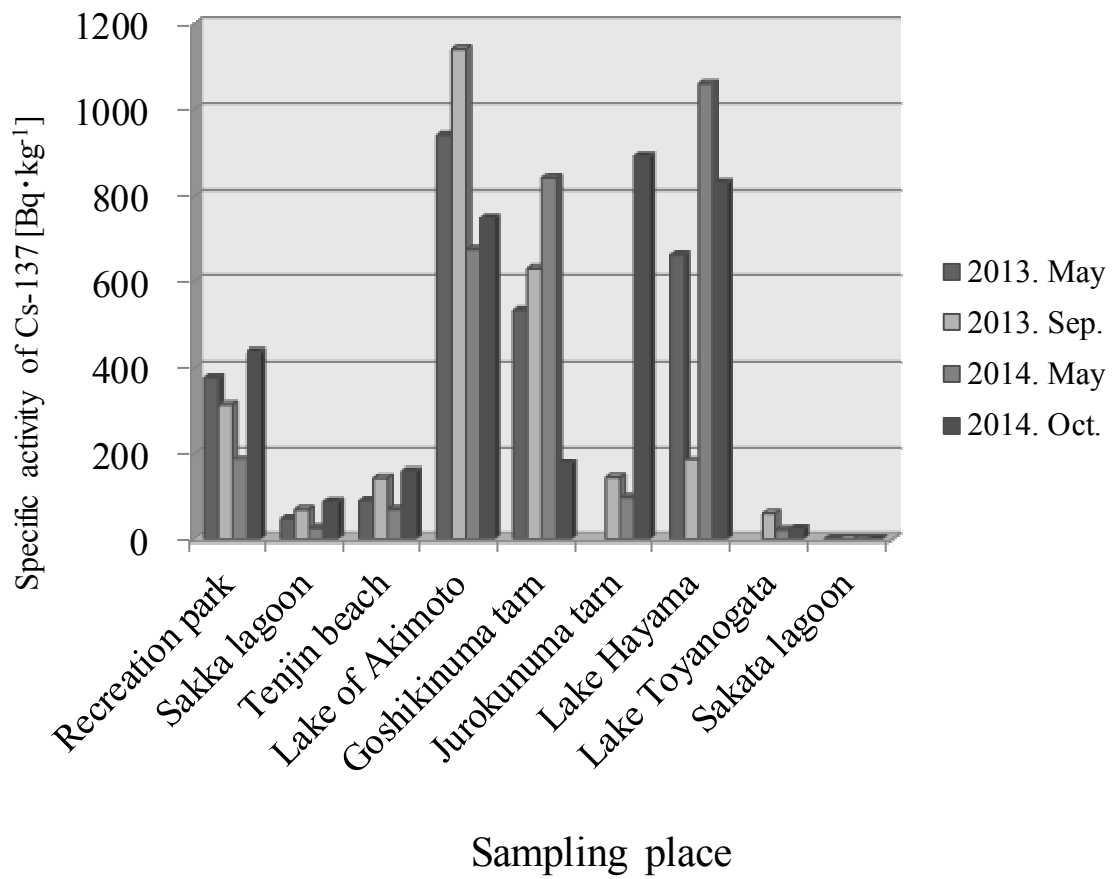


Fig.3.7 Specific activity of Cs-137 in Fukushima and Niigata

CHAPTER 4

**Based on the Estimation of Effect of Tritium on
Human Body by Applying Hydrogen Isotope
Exchange Reaction**

4.1 Introduction

The external exposure from tritium (T) can be neglected because the maximum energy of the emitted β -ray is very low (18.6keV). In the case of HTO, T can be incorporated into the body and behaves as free water tritium (FWT)⁷⁾. T also causes a hydrogen isotope exchange reaction⁸⁾ (T-for-H exchange reaction) that can be divided into exchangeable organically bound tritium (OBT) and non-exchangeable OBT⁹⁾. Exchangeable OBT behaves as FWT in the body, and the dose coefficient of T in FWT is unity. On the other hand, the dose coefficient of T in non-exchangeable OBT is 2.3¹⁰⁾. This is a key distinction that makes the study on the internal exposure of T and is very important. The T concentration in the atmosphere will increase as more reprocessing plants for spent nuclear fuel come online and nuclear fusion research continues. Thus, the study on exchangeable OBT and non-exchangeable OBT is more important.

Previously¹¹⁾, we have studied the T-for-H exchange reaction over the range of 50~70°C using the A'' -McKay plot method, and the rate constants (k) of the materials were obtained. We also have estimated the reactivity of functional groups using the k . Considering the evaluation of internal

exposure, it is found that observing the T-for-H exchange reaction under the biological temperature ($\approx 36^\circ\text{C}$) in a heterogeneous system is necessary¹²⁾.

Taking into account the above background information, the T-for-H exchange reaction (gas-solid reaction) between HTO vapor and each amino acid having two different kinds of functional groups (*i.e.*, COOH and NH₂ groups) is observed at 36 °C and 25 °C. The observed data were applied to the A'' -McKay plot method to obtain the k for the functional groups in each amino acid. Each Taft plot was also drawn by using these k values. Consequently, the ratio of the polar effect to the steric effect in the reaction can be estimated. Observing the reaction at various temperatures, the temperature dependence is clarified. Also the polar substituent constant and the steric substituent constant were calculated from the Taft's plot. The differences between extrapolation values from obtained Arrhenius plots for the several functional groups and experimental values were evaluated. From these experiments, the effect of T on the human body can be estimated.

4.2 Theoretical Background

As mentioned in previous literature¹²⁻¹⁷⁾, the A'' -McKay

plot is described by the following equation.

$$kt = -\log_{10} [1 - x/x_{\infty(F)}] \quad (1)$$

k : rate constant

t : time

x : activity observed (for the solid sample in the reaction)

$x_{\infty(F)}$: calculated activity (for the solid sample)

This method has three characteristics: (1) The value of the slope equals k when the plot of $-\log_{10} [1 - x/x_{\infty(F)}]$ vs. t is drawn. (2) k can be also obtained in a heterogeneous system. (3) It is possible to study the reactivity of the materials not only having one (or the same kind of) functional group(s), but having three different kinds of functional groups.

4.3. Experimental

Using a vacuum line¹⁸⁾, each T-for-H exchange reaction was observed between HTO vapor and several amino acids at 25, 36, 50, 60, or 70°C. Each solid sample was sufficiently powdered in an agate mortar, then dried and sieved to obtain a grain size between 53 and 75 μm in diameter¹⁸⁾. For each reaction run, both 7.22 mg of HTO water as a gas sample (whose specific activity was $8 \times 10^5 \text{ Bq} \cdot \text{g}^{-1}$) and 15.0 mg of each solid material were used. The method of observation was the same as

previously reported¹⁸⁾. After the reaction, the solid sample was dissolved in 3.00 ml of water, and the activity of 1.00 ml of the solution was measured with a liquid scintillation counter. Because the half-life of T is 12.3 years, the activity was corrected by a calculation every three months.

In order to apply the obtained data to the A'' -McKay plot method in the gas-solid reaction, the excess experiment^{19, 20)} was performed. From the experiment, it is found that the total number of ^1H atoms and T atoms in this HTO vapor are much larger than the total number of H atoms at the solid sample surface contributing to the reaction. In other words, we changed the mass of the solid samples in order to use the analysis method of pseudo first order reaction.

Based on the two previous reports^{21), 22)}, ^1H atoms directly bonded to the carbon atom cannot participate in the reaction. Accordingly, it is found that the exchange ^1H atoms are the only ^1H atoms in the COOH and NH_2 groups under the conditions in this work.

4.4. Results and discussion

4.4.1 Applicability of the A'' -McKay plot method

Based on the former section, the excess experiment was

carried out. If the excess condition is satisfied, total activity of each solid sample materials is proportional to the mass in the reaction. **Figure 4.1** shows the excess experiment of the L-aminobutylic acid at 70 °C. This figure shows a linear relationship between the activity and mass. That is, the number of reactions per unit is constant in the mass range of 5~60 mg and the quantity of the HTO vapor is much in excess to the L-aminobutylic acid. The results obtained by using other sample materials were similar to that of the amino acid.

4.4.2 Reactivity of each material

The T-for-H exchange reaction between HTO vapor and each amino acid was observed. The relation between reaction time and the specific activity of L-aminobutylic acid at 25°C was drawn (**Fig. 4.2**). It is found that the reaction occurred because the specific activity of T increased with time. From the previous report²³⁾, it can be assumed that the reactivity of the COOH group is larger than that of the NH₂ group in the same molecule. Therefore, it found that the three following reactions occurred in this figure.

Part (1) : From the origin to (A)

Both the COOH group and NH₂ group at the surface of L-aminobutylic acid react with HTO vapor, and a reaction at the surface of the COOH group reaches equilibrium at (A).

Part (2) : From (A) to (B)

Only the NH₂ group at the surface of L-aminobutylic acid reacts with HTO vapor and a reaction at the surface of the NH₂ group reaches equilibrium at (B).

Part (3) : After (B)

T on the solid surface diffuses to the inside.

4.4.3 Reactivity of COOH and NH₂ groups in each material

In Fig. 4.2, the data obtained from Part (1) was applied to the A''-McKay plot method to obtain the rate constant (k_{NH_2})¹⁸). **Figure 4.3** shows the A''-McKay plot of the NH₂ group, and the slope of the straight line of the NH₂ group is equal to k_{NH_2} . In order to obtain the rate constant (k_{COOH}), the reaction value of the NH₂ group in Part (1) was calculated from the broken line. Then the reaction value of the NH₂ group thus obtained was subtracted from the total reaction value. Each data thus obtained was applied to the A''-McKay plot method in order to obtain k_{COOH} . The slope of the straight line of the COOH group in Fig. 4.3 is equal to k_{COOH} . For other materials, the values of k for the

COOH and NH₂ groups are shown in Table 4.1. The table shows that the reactivity of each group increases with increasing temperature. In this way, the *A''*-McKay plot method is useful to analyze two steps of a simultaneous reaction.

Using these *k* values, Arrhenius plots for both the COOH and NH₂ groups are shown in **Fig. 4.4**. The correlation coefficients of the straight lines in the figure satisfy the condition of significance at the 1% level. As previously reported²⁴⁾, linearity was seen in the range of 50 ~ 70 °C. However, such linearity was not obtained at low temperature. In this work, linearity was obtained over the range of 25 ~ 70 °C, that is, the reactivity at biological temperature can be clarified. In addition, activation energies (*E_a*) for both COOH and NH₂ groups were obtained from Fig. 4.4 and shown in Table 4.1.

4.4.4 Applicability of Taft's equation

In order to quantitatively estimate the reactivity, we applied the *k* values to Taft's equation²⁵⁾. Taft's equation is generally expressed as follows:

$$\log_{10}(k/k_0) = \rho^* \sigma^* + \delta E_s \quad (2)$$

In this work, k_0 is the rate constant for glycine; k is a rate constant for each amino acid; ρ^* equals the reaction constant for amino acids; σ^* equals the polar substituent constant; E_s equals the steric substituent constant; δ is a measure of the steric effect. The following two operations were carried out: (1) the value of ρ^* was changed from 0.0 to 1.0 at 0.1 intervals; (2) inversely, δ was changed from 1.0 to 0.0 at 0.1 intervals. As a result, eleven figures for the COOH group (or the NH₂ group) can be obtained at each temperature. One line was obtained in each figure, and the line having the largest correlation coefficient out of the eleven lines was selected as the ratio of ρ^* to δ for the functional group at each temperature. These ratios for the COOH and NH₂ groups at 25°C, 36°C, and 50°C are shown in Table 4.2, and the plots having the largest correlation coefficient for COOH and NH₂ groups at 25°C are shown in **Figs. 4.5 and 4.6**. It is fairly certain that (1) the reactivity of amino acids follows Taft's equation in gas-solid reaction, (2) the COOH group is strongly influenced by the steric effect, and (3) the NH₂ group is strongly influenced by the polar effect. Consequently, the effect of "the ratio of the polar effect to the steric effect" on the reactivity of the materials has been clarified at each temperature.

4.4.5 Comparison of the reactivity of NH₂ group in each amino acid

Comparing the structures of the various amino acids having two functional groups (COOH and NH₂), the number of carbon or benzene rings is different in L-glycine as shown Table 4.1. Based on Taft's equation mentioned in the former section, the NH₂ group can be considered as having some polar effect. The CH₃ group is an electron-donative substituent ($-I$ effect¹⁸) and the effect increases with increasing carbon chain. If electron density of the functional group becomes large, the reactivity generally diminishes. Therefore, the reactivity of the NH₂ group of L-norvaline diminishes because it has the longest carbon chains in the sample materials. In addition, by comparison between L-norvaline and L-valine, it is found that the reactivity tends to diminish by existing carbon near the functional group. However, the C₆H₅ group is an electron attractive substituent ($+I$ effect). So, electron density of the functional group diminishes, and the reactivity of the NH₂ group of L-phenylalanine or L-phenylglycine is larger than that of L-glycine.

On the other hand, the COOH group is also influenced by the steric effect. Based on the influence of steric effect of the substituent, the reactivity of the COOH group is diminished.

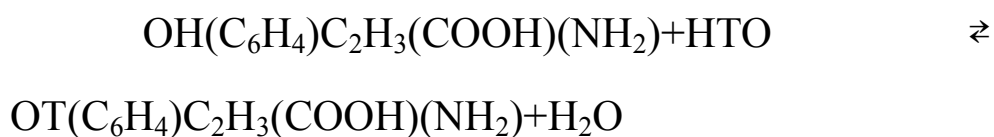
Because the +I effect of the benzene ring is larger than the -I effect of CH₃ group, the reactivity of L-phenylalanine or L-phenylglycine is similar to that of L-glycine (in spite of having the polar effect). That is, the reactivity of the COOH group diminishes because the volume of the substituent becomes large.

4.4.6 Reactivity of L-tyrosine

The T-for-H exchange reaction between HTO vapor and L-tyrosine was observed. The relation between reaction time and the specific activity of L-tyrosine acid at 25°C was shown (Fig. 4.7). The plot shows three inflections, and the reaction is separated into 3 parts as follows.

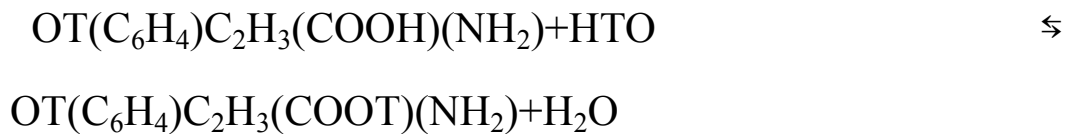
Part (1): From the origin to (A)

The T-for-H exchange reaction proceeds between OH, COOH and NH₂ group of L-tyrosine and HTO vapor at the surface area. A reaction at surface area of OH group reaches equilibrium at (A) as follows.



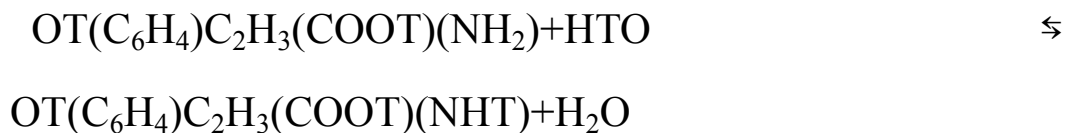
Part (2): From (A) to (B)

The T-for-H exchange reaction proceeds between COOH and NH₂ group of L-tyrosine and HTO vapor at the surface area. A reaction at surface area of COOH group reaches equilibrium at (B) as follows.



Part (3): From (B) to (C)

The T-for-H exchange reaction proceeds only NH₂ between group of L-tyrosine and HTO vapor at the surface area. A reaction at surface area of NH₂ group reaches equilibrium at (C) as follows.



After (C), the activity of T refers to inner diffusion reaction.

4.4.7 Application of A'' -McKay plot method

To obtain the k , the data from part 1 to 3 were applied to A'' -McKay plot method. The method to calculate k is the same as the article²³⁾. Figure 4.8 shows the A'' -McKay plots of

L-tyrosine at 25°C and the correlation coefficient for the straight line of the plots are 1%. Table 4.4 indicates the each k .

4.4.8 Extrapolation values (k_{ex}) on the Arrhenius plot

Previously²⁴⁾, we drew the Arrhenius plot for L-tyrosine in the range of 50 ~ 70°C. Using the plot, the rate constants of L-tyrosine in 25 and 36°C were obtained (Fig. 4.9). The extrapolation values (k_{ex}) and experimental values (k) are indicated in Table 4.4. From the table, there was little difference between k_{ex} and k . In other words, it is possible to analogize the k at low temperature using the Arrhenius plot in the range of 50 ~ 70°C. Consequently, the value of k_{ex} can be regarded as the value of k . Therefore, all of the data (shown in Table 4.4) at body-temperature can be obtained by using the data at room temperature.

4.4.9 Applicability of Taft's equation

In order to quantitatively estimate the reactivity, we applied the k values to Taft's equation.

The Taft's plots about NH₂ and COOH group were drawn (Figs. 4.5, 6). Using these Taft's plots, the polar substituent constant

(σ^*) and the steric substituent constant (E_s) of C_7H_7O can be analogized. At $25^\circ C$, the following values were indicated previously²⁶⁾: for COOH group ; $\rho^*=0.2$, $\delta=0.8$, $k_0=3.9$; for NH_2 group ; $\rho^*=0.9$, $\delta=0.1$, $k_0=3.3$, and the followings are obtained in this works : for COOH group ; $k=5.8$; for NH_2 group ; $k=2.4$. As a results, the calculated values of σ^* and E_s were obtained (Table 4.5). These obtained values can clarify the reactivity of the T-for-H exchange reaction having the substituent (C_7H_7O) like L-tyrosine.

4.4.10 The influence of the substituent to the reactivity in L-tyrosine

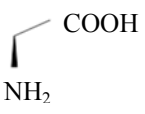
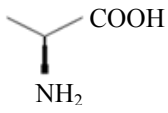
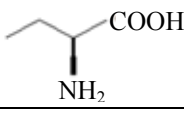
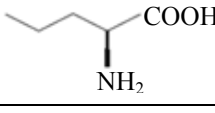
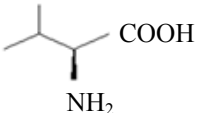
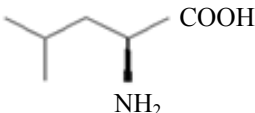
The substituent (C_7H_7O) of L-tyrosine influences COOH and NH_2 groups. The influences which affect COOH and NH_2 groups are polar effect and steric one. As mentioned above, $\sigma^*=-0,182$ is affected by an electron attractive substituent(+I effect), and the reactivity of T-for-H exchange reaction increases compared to the material without a substituent. In addition, $E_s=0.44$ means a steric hindrance in the T-for-H exchange reaction. That is, the reactivity with substituent is less than the material without the substituent. In this study, the quantitative

evaluation of the reactivity of the T-for-H exchange reaction can be conducted using polar and steric substituent constants.

4.5. Conclusion

The T-for-H exchange reaction (gas-solid reaction) between HTO vapor and each amino acid was observed and the reactivity of the amino acid was quantitatively analyzed. The Arrhenius plots have good linearity over the range of 25~70°C. Based on these results we can make the following statements. (1) The reactivity of some amino compounds at biological temperature was clarified. (2) Applying Taft's equation, the ratio of polar effect to steric effect was clarified at each temperature (i.e., 25°C and 36°C). (3) Using the Arrhenius plot, the rate constants of these amino compounds can be evaluated. (4) Applying Taft's equation, polar and steric substituent constants of L-tyrosine were obtained and the reactivity of the T-for-H exchange reaction was quantitatively observed. (5) The method used in this work can quantitatively clarify the reactivity of the T-for-H exchange reaction, and can be useful to estimate the internal exposure of exchangeable OBT.

Table 4.1 Rate constants (k) for COOH and NH₂ groups in each sample material and activation energy (E_a)

Material formula	Structural		$k/10^{-2} \text{ h}^{-1}$					E_a kJ·mol ⁻¹
			25°C	36°C	50°C	60°C	70°C	
L-glycine ²¹⁾		k_{NH_2}	3.3	3.9	5.9	7.2	8.2	18
		k_{COOH}	3.9	5.4	10	11	13	24
L- α -alanine ²¹⁾		k_{NH_2}	3.1	3.7	5.3	8.4	12.5	26
		k_{COOH}	3.8	5.3	14	20	37	44
L-aminobutyric acid		k_{NH_2}	2.7	3.5	5.6	7.3	8.5	23
		k_{COOH}	3.7	5.1	12	17	21	35
L-norvaline ²³⁾		k_{NH_2}	2.5	3.3	5.5	7.3	7.9	23
		k_{COOH}	3.6	4.8	11	16	20	35
L-valine		k_{NH_2}	2.3	3.0	5.3	6.7	7.5	24
		k_{COOH}	3.3	4.2	10	15	17	34
L-leucine		k_{NH_2}	2.4	3.2	5.4	6.9	7.7	24
		k_{COOH}	3.5	4.5	11	16	19	35

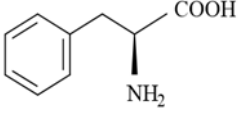
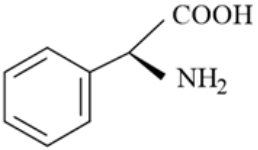
L-2-phenylglycine ²⁴⁾		k_{NH_2}	3.5	4.0	6.0	7.6	8.7	18
	k_{COOH}	3.7	5.6	14	17	18	33	
	L-2-phenylalanine ²⁴⁾		k_{NH_2}	3.4	4.0	5.8	7.6	8.2
	k_{COOH}	3.9	5.6	14	16	18	33	

Table 4.2 The ratio of the reaction constant (ρ^*) to the steric effect (δ).

Temperature	Functional group	ρ^*	δ
25°C	COOH	2	8
	NH ₂	9	1
36°C	COOH	4	6
	NH ₂	8	2
50°C	COOH	3	7
	NH ₂	10	0
60°C	COOH	3	7
	NH ₂	10	0
70°C	COOH	3	7
	NH ₂	10	0

Table 4.3 Solid material used in this work

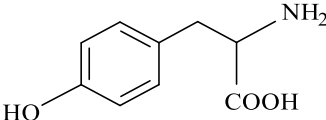
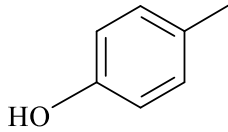
Solid material	Structural formula	Purity
L-tyrosine	 <chem>N[C@@H](Cc1ccc(O)cc1)C(=O)O</chem>	>98.5%

Table 4.4 Rate constants (k_{ex} and k) for OH, COOH and NH₂ groups in L-tyrosine

Rate constant	$k / 10^{-2} \text{h}^{-1}$		
	25 °C	36 °C	
k_{ex} (extrapolation value)	k_{OH}	7.5	7.8
	k_{COOH}	5.8	6.0
	k_{NH_2}	2.4	2.4
k (experimental value)	k_{OH}	7.5	10
	k_{COOH}	5.7	7.0
	k_{NH_2}	2.5	3.5

Table 4.5 Polar substituent constant (σ^*) and steric substituent constant (E_s) of C₇H₇O

Compositional formula	Structural formula	σ^*	E_s
C ₇ H ₇ O		-0,182	0.44

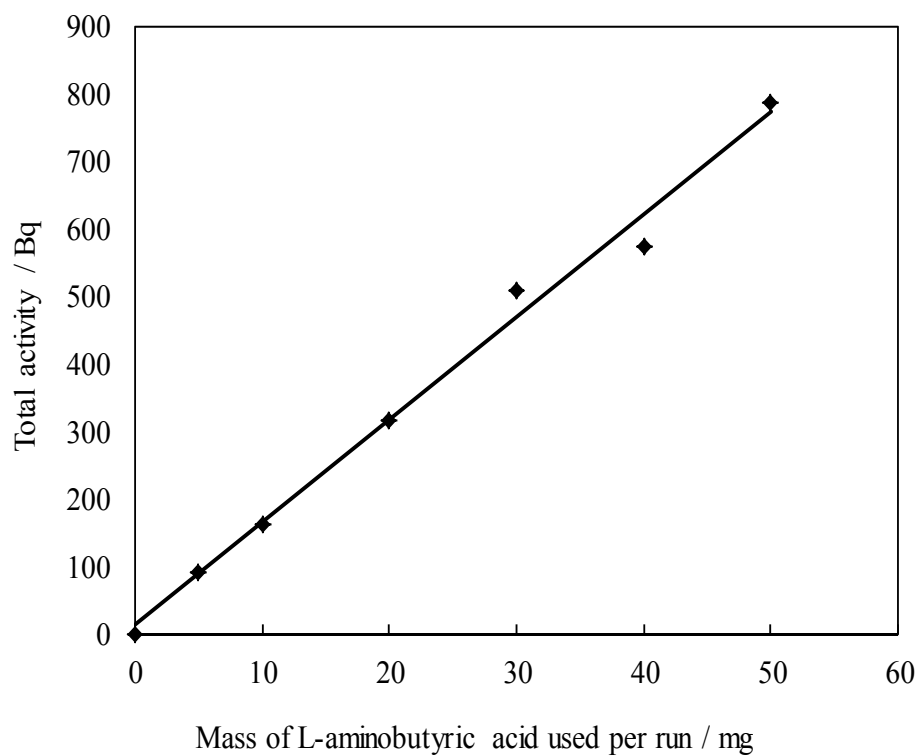


Fig.4.1 Activity of L-aminobutyric acid vs. mass of the material for the reaction.
Gas sample material : HTO vapor
Reaction temp. : 70 °C
Reaction time : 1.0 h

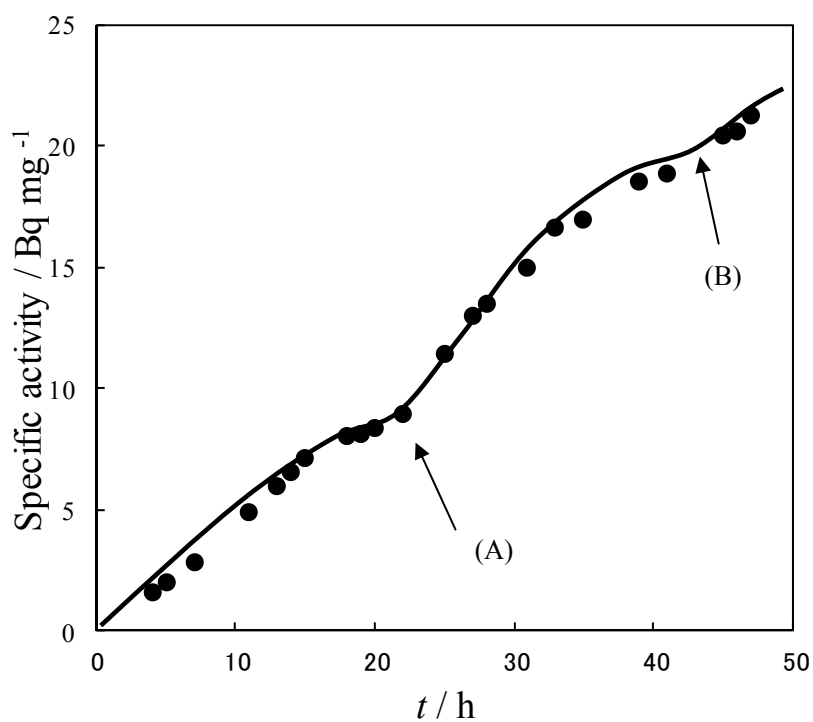


Fig.4.2 T specific activity vs. time for the reaction between L-aminobutyric acid and HTO vapor.
Reaction temp. : 25 °C

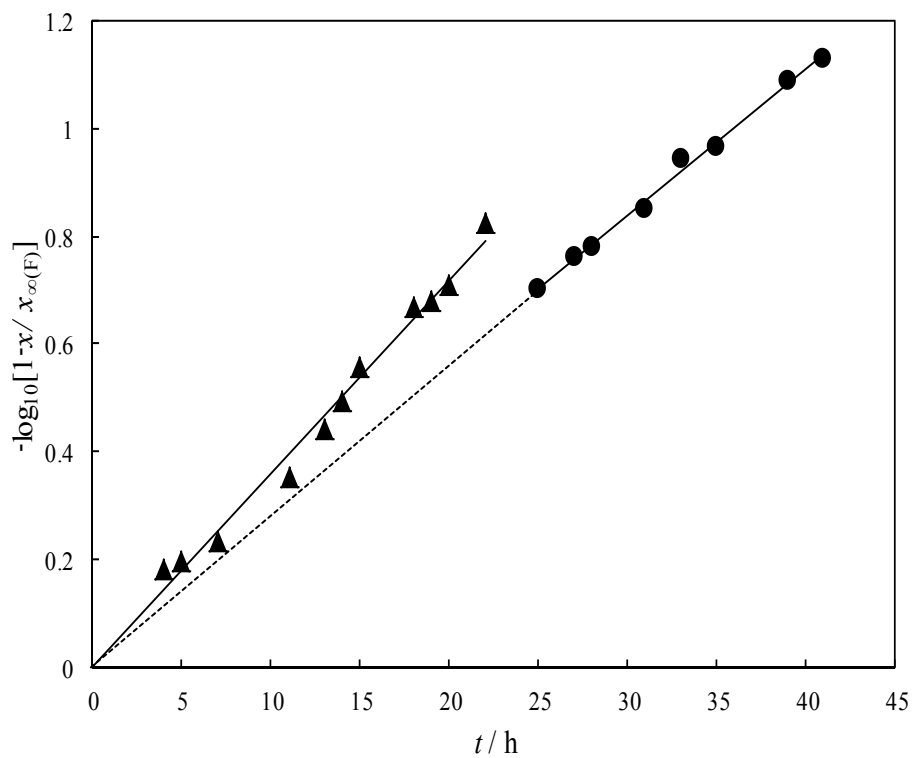


Fig.4.3 A'' -McKay plots for L-aminobutyric acid in the reaction at 25°C.

▲: COOH group, ● : NH₂ group

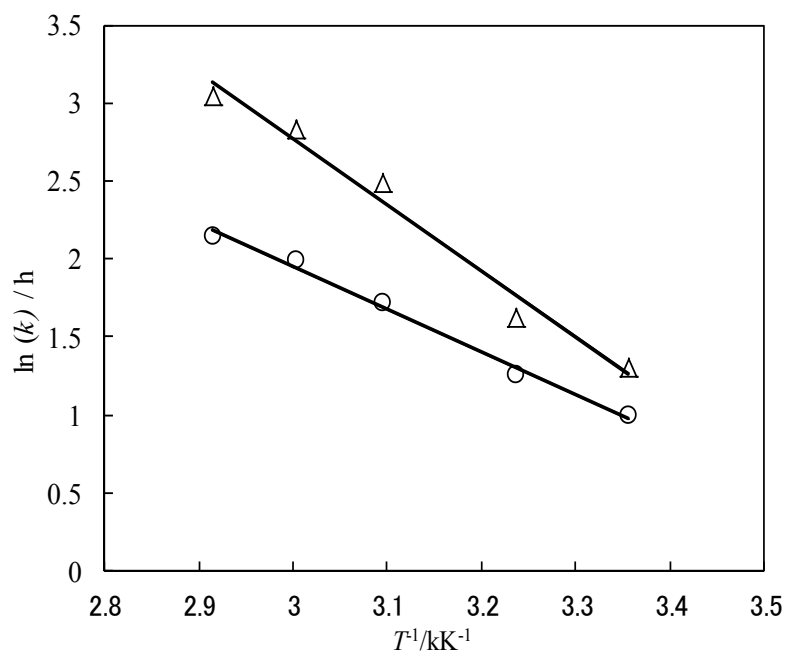


Fig.4.4 Arrhenius plots for the COOH and NH₂ groups in L-aminobutyric acid.

Δ : COOH group, \circ : NH₂ group

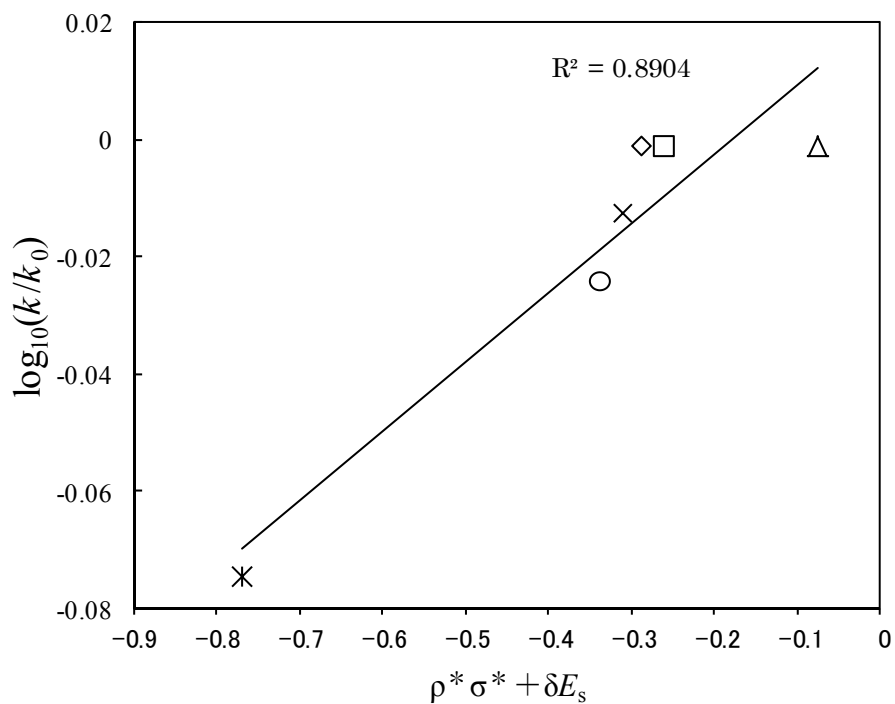


Fig.4.5 A plot (based on Taft's equation) of
COOH group for each amino acid.
Reaction temp : 25 °C

× : L-aminobutyric acid(obtained in this work)

* : L-valine(obtained in this work)

□ : L-2-phenylglycine

◇ : L-phenylalanine

△ : L- α -alanine

○ : L-norvaline

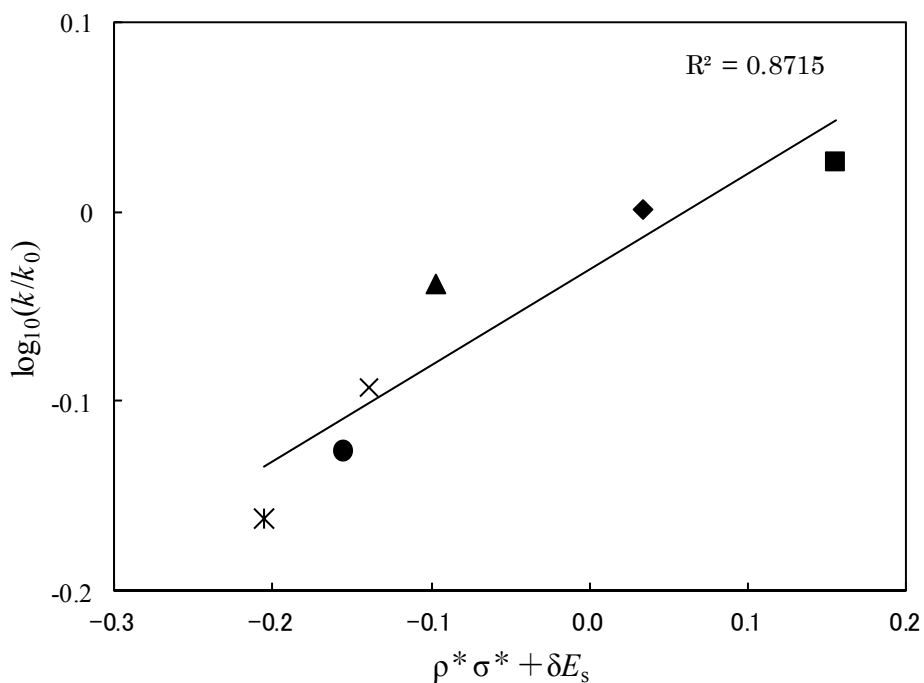


Fig.4.6 A plot (based on Taft's equation) of NH_2 group for each amino acid.
Reaction temp : 25 °C

× : L-aminobutyric acid

* : L-valine

■ : L-2-phenylglycine

◆ : L-phenylalanine

▲ : L- α -alanine

● : L-norvaline

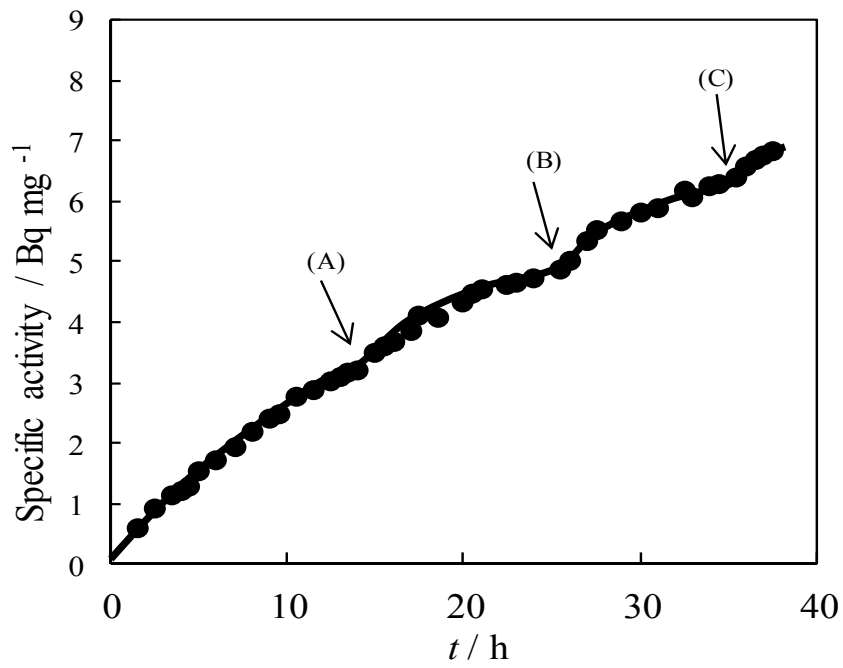


Fig.4.7 Specific activity vs. time for the reaction between L-tyrosine and HTO vapor at 25°C.

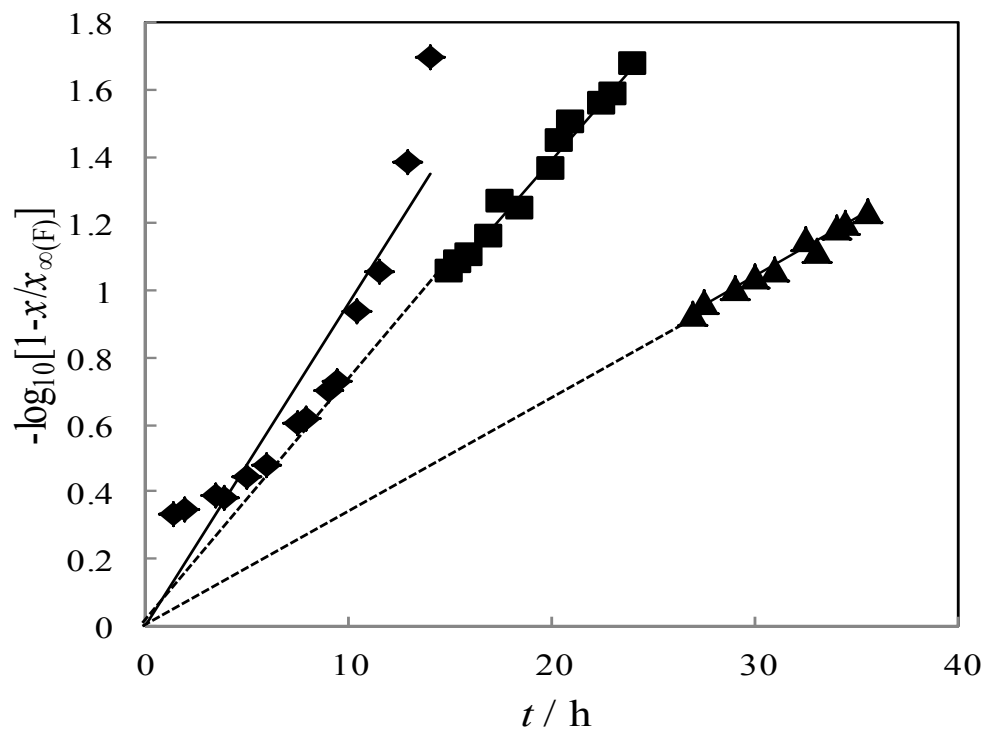


Fig.4.8 A'' -McKay plots for the several functional groups in L-tyrosine.
 ■ : OH, ◆ : COOH, ▲ : NH₂

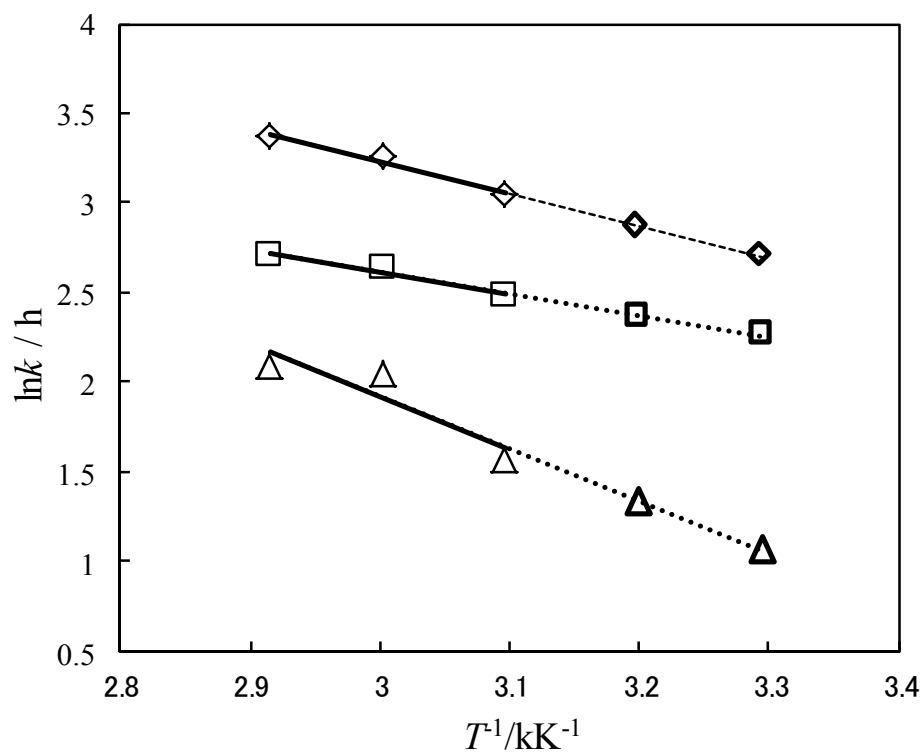


Fig.4.9 Arrhenius plots for the OH, COOH and NH₂ groups and extrapolated evaluation in L-tyrosine.

\diamond : OH group, \square : COOH group, \triangle : NH₂ group

CHAPTER 5

Method of Estimation of the Internal Exposure of Tritium in Biomolecule by Applying the Hydrogen Isotope Exchange Reaction

5.1 Introduction

T can be classified into FWT and OBT. In addition, OBT can be classified into exchangeable OBT and non-exchangeable OBT. Exchangeable OBT is easy to cause hydrogen exchange reaction, but non-exchangeable OBT is not easy to cause hydrogen exchange reaction. As current problems, Distinction of exchangeable OBT and non-exchangeable OBT is vague. Furthermore, Evaluation for the internal exposure of T is only metabolism, but was not considered exchange reaction. Indeed, evaluation of the hydrogen isotope exchange reaction is not accomplished.

In this study, the reactivity of hydrogen exchange reaction for Exchangeable OBT and non-exchangeable OBT was observed. In addition, the reverse reaction occurs between these samples labelled by tritium and H₂O.

5.2 Experimental

Table 5.1 shows the used material and chemical structural formula. The method of experimental is the same one of CHAPTER4.

5.3 Result and discussion

5.3.1 Up take reaction

The T-for-H exchange reaction between HTO vapor and (Sodium octanoate or Sodium benzoate) was observed. The relation between reaction time and the specific activity of Sodium Octanoate at 70°C was drawn (**Fig. 5.1**). And figure 5.2 shows the A'' -McKay plots of Sodium octanoate at 70°C and the correlation coefficient for the straight line of the plots are 1%. Table 1 indicates the each k .

5.3.2 Elimination reaction

The H-for-T exchange reaction between H₂O vapor and (tritium labelling Sodium octanoate or Sodium benzoate) was observed. The relation between reaction time and the specific activity of Sodium Octanoate at 70°C was drawn (**Fig. 5.3**). Figure 5.4 shows the A'' -McKay plots of Sodium octanoate at 70°C and the correlation coefficient for the straight line of the plots are 1%. Table 1 indicates the each k .

5.3.3 Equilibrium reaction

From Fig.5.1 and Fig.5.3, the specific activity of T on equilibrium at is 1Bq/mg. Because the concentration of T in HTO vapor is 800Bq/mg, the equilibrium constant is 0.00125.

5.3.4 Evaluation of the reactivity

From the table 5.1, each k of uptake and elimination for L-tyrosine is the same. On the other hand, about non-exchangeable OBT the k of uptake is larger than that of elimination. The ratio is 15%~25%. Indeed, non-exchangeable OBT is easy to remain in sample.

5.3.4 Evaluation of the internal exposure

From above the mentioned, it is found that non-exchangeable OBT is easy to remain in hydrogen isotope exchange reaction. Because Evaluation of internal exposure of T is only interest of metabolism at present, it is necessary to consider hydrogen isotope exchange reaction. In our body, water and protein is contained 70% and 16%, respectively. Hydrogen isotope exchange reaction from the water to protein must be considered

because the main intake course of T is water. Protein is produced by amino acids, the main amino acids is shown Table 5.2. The number of C-H bound in these amino acids and of O-H bound in water is counted in our body (60kg). The number of aliphatic and aromatic C-H bound is 1.39×10^{25} and 0.730×10^{25} , respectively. O-H bound of water is 14×10^{28} . The ratio of the number O-H bound in water to the number of aliphatic and aromatic C-H bound in an amino acid is 0.992% and 0.552%, respectively. From the following equation, transfer coefficient of T about hydrogen isotope exchange reaction was obtained.

$$(0.00992 \times 0.15 + 0.00552 \times 0.24) \times 0.00125 \times 20 = 0.000070$$

Transfer coefficient of T from FWT to non-exchangeable OBT is 0.000070. When internal exposure of T is calculated applying the transfer coefficient, the amount of increase in dose is only $1.3 \times 10^{-11} \mu\text{ Sv}$. On the other hand, the air dose is $0.1 \mu\text{ Sv/h}$ in Niigata city. Therefore, the dose of hydrogen isotope exchange reaction in human body can be ignored because the dose is very small.

5.4 Conclusions

The T-for-H exchange reaction (gas-solid reaction) between HTO vapor and L-tyrosine was observed, and the reactivities of the Sodium octanoate or Sodium benzoate were quantitatively analyzed. Based on these results, the following statements can be obtained. (1) It is found that non-exchangeable OBT is easy to remain in hydrogen isotope exchange reaction. (2) The transfer coefficient of T from FWT to non-exchangeable OBT is 0.000070. (3) When internal exposure of T is calculated applying the transfer coefficient, the amount of increase in dose is only $1.2 \times 10^{-8} \mu \text{ Sv}$. (4) The dose of hydrogen isotope exchange reaction in human body can be ignored because the dose is very small.

The part of this study was presented at the 51th Annual Meeting on Radioisotope and Radiation Research held in Tokyo University.

Table 5.1 Rate constants (k) for uptake and elimination reaction (T-for-H exchange reaction) in each sample material at 70 °C

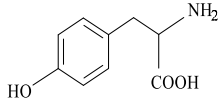
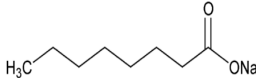
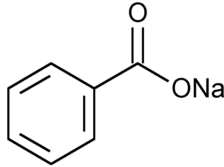
		$k / 10^{-2} \text{h}^{-1}$				
Material		36 °C		70 °C		
		k (uptake)	k (eliminate)	k (uptake)	k (eliminate)	
Exchangeable OBT	L-tyrosine	k_{OH}	11	11	29	14
		k_{COOH}	15	15	15	14
		k_{NH_2}	12	12	8.1	8.1
Non-Exchangeable OBT	n-Sodium Octanoate	$k_{\text{C-H}}$	0.19	0.14	0.54	0.46
						
Non-Exchangeable OBT	Sodium benzoate	$k_{\text{C-H}}$	0.22	0.18	0.71	0.54
						

Table 5.2 Main amino acids

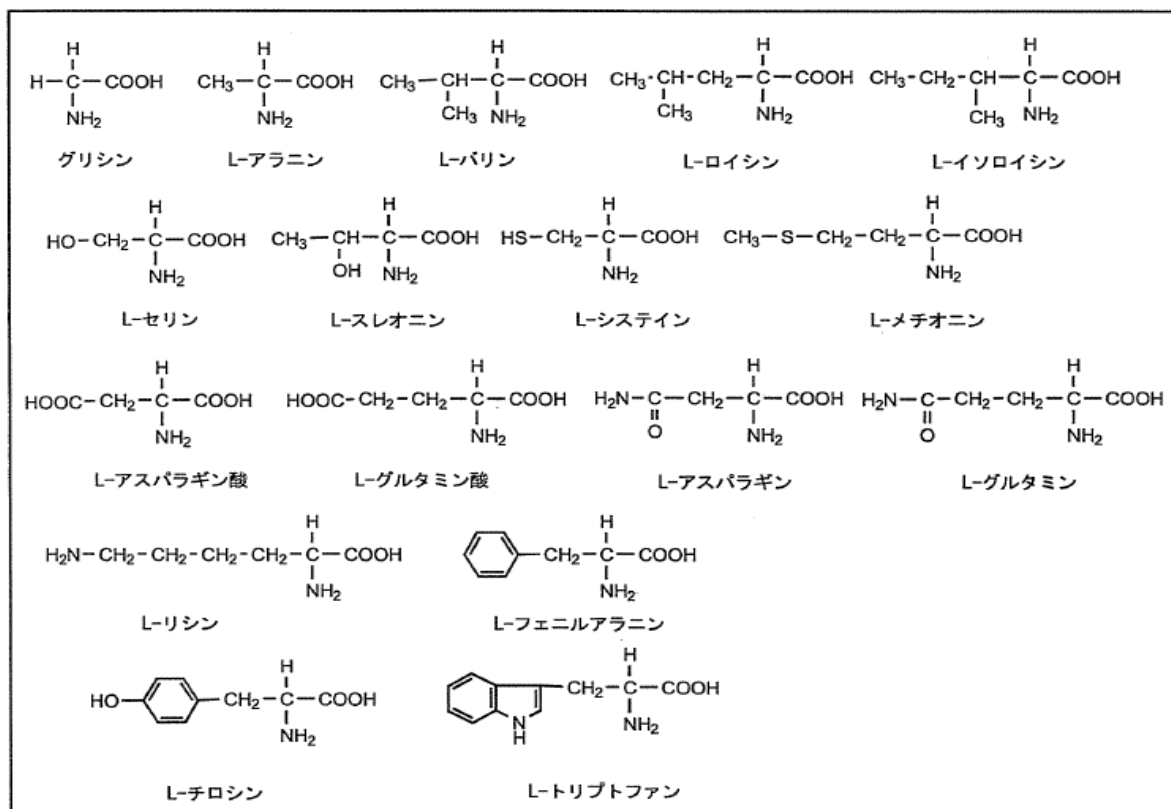


図1 タンパク質を構成する代表的なα-アミノ酸の構造

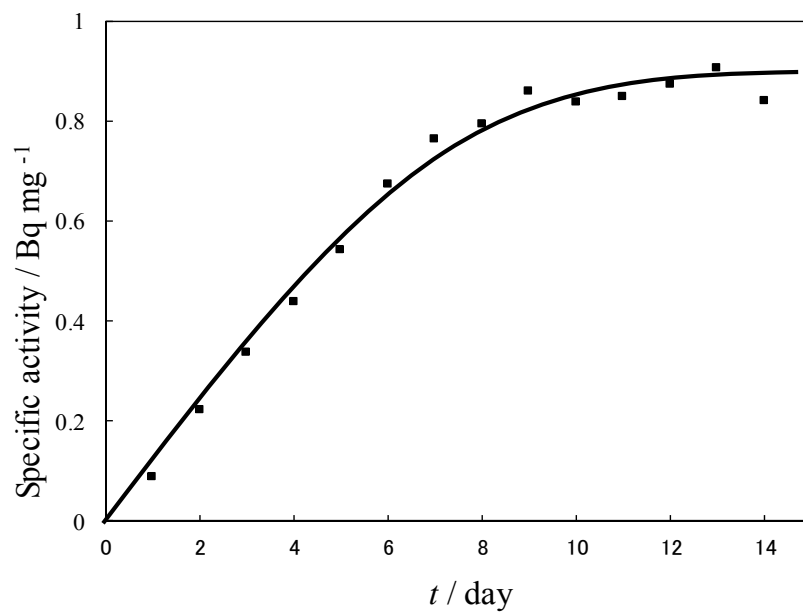


Fig.5.1 Specific activity vs. time for the reaction between Sodium octanoate and HTO vapor. Reaction temp : 70 °C

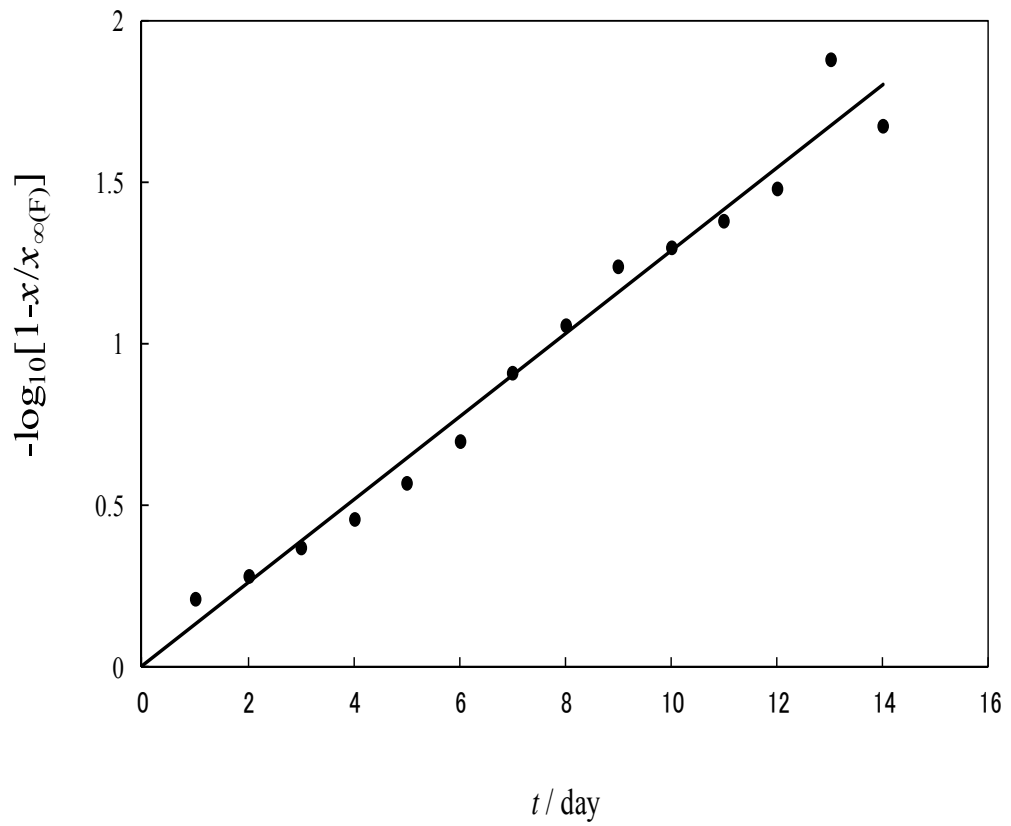


Fig.5.2 A'' -McKay plot Sodium octanoate in the reaction at 70°C.

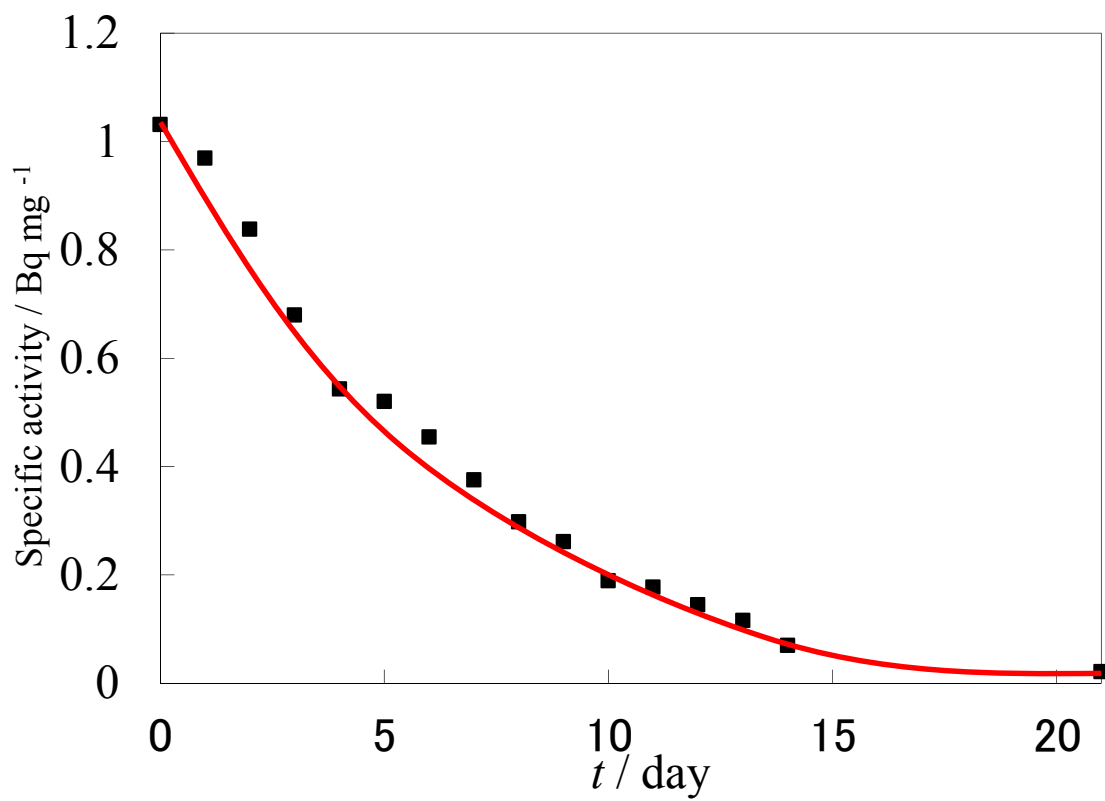


Fig.5.3 Specific activity vs. time for the exchange reaction between Sodium octanoate and H₂O vapor.
Reaction temp : 70 °C

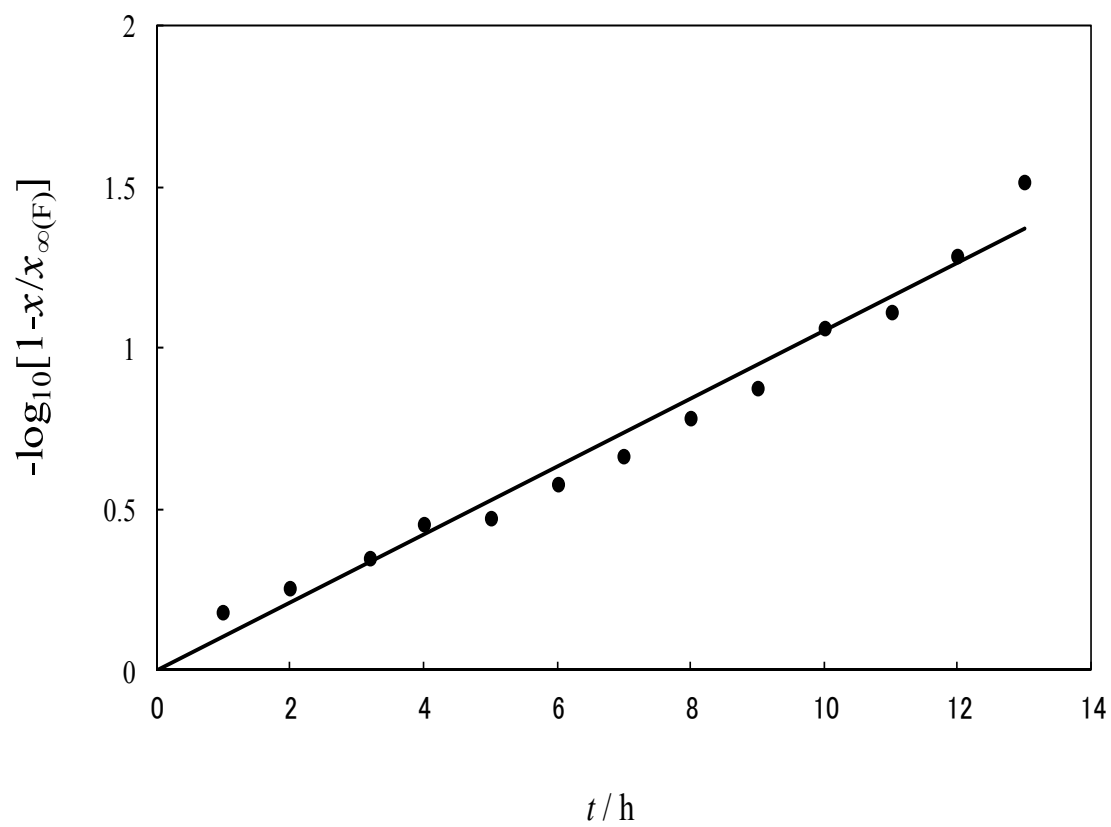


Fig.5.4 *A''*-McKay plot of elimination reaction of Sodium octanoate in the reaction at 70°C.

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