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# Present State and Future Subjects of Tritium Measuring Techniques

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## Abstract

A tritium measuring technique is one of key technologies for the precise control and safe handling of fuel particles in the fusion systems. A variety of techniques have been already established so far for measurements of low-level tritium such as a tracer of chemical reactions and environmental tritium. However, high-level and huge amount of tritium is applied to the fusion reactors. Some techniques developed so far are applicable for fusion environment, but new techniques will be also required for establishment of a tritium plant in future fusion reactors. From this viewpoint, application of β-ray-induced X-ray spectrometer (BIXS) for highly tritiated waters is described with the conventional devices, where the BIXS was newly developed by author to measure high-level tritium *in-situ*. Present state and future subjects of tritium measuring techniques will be discussed in this paper.

**Key words**: tritium, high concentration, measurement technique, BIXS, fusion reactor

## I. Introduction

It is indispensable to establish the techniques for precise control of tritium species from view points of safe handling and economy of high-level tritium in the future fusion reactors. For this reason, applicability of a variety of the present measuring techniques has been examined for high-level tritium in gaseous and/or liquid state. Furthermore, research and development of new measuring techniques have been conducted so far to determine precisely the amount or concentration of tritium.

Most of these techniques, however, have no examination exposed to high-level tritium over a long period. Stability of the measuring devices is very important to control the concentration and/or amount of

Table 1. Major physical properties of a tritium atom.

| Physical Properties | Values |
|---|---|
| Decay Scheme | $^3H \longrightarrow {}^3He + \beta^- + \bar{\nu}$ |
| Mass of $^3H$ | 3.0160492$\underline{7}$ g/mol |
| Maximum Energy of β-rays | 18.59 keV |
| Average Energy of β-rays | 5.70 keV |
| Mode Energy of β-rays | 2.50 keV |
| Total Energy of β-rays | 33.8 mW/Ci |
| Half-life | 12.32 y (4500 d) |
| Decay Constant | $1.783 \times 10^{-9}$ $s^{-1}$ |
| Specific Activity | 2.146 PBq/mol |
| Maximum Range of β-rays | *ca.* 6 μm in water |
| Recoil Energy of $^3He$ | 3.4 eV |
| Ionization Energy of $^3H$ | 15.5 eV |

tritium in a fusion reactor. In addition, high durability as well as high performance is required to the measuring devices under the severe conditions in a fusion reactor. From these viewpoints, present state and future subjects of tritium measuring techniques toward establishment of a fusion reactor will be discussed in this paper.

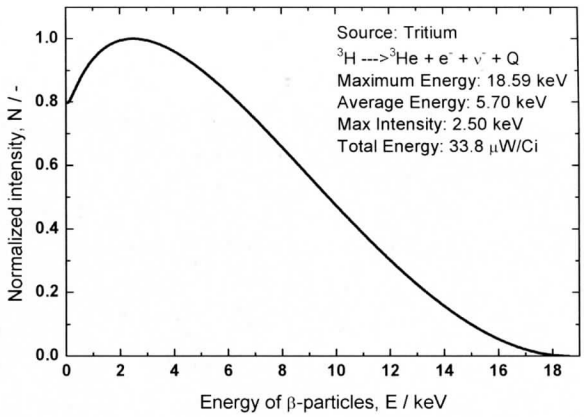


Fig. 1 Energy spectrum of tritium β-rays.

## II. Basic Properties of Tritium

Physical properties of a tritium atom have been clarified as shown in Table 1. When tritium atoms decay, β-rays are emitted from nuclei. The energy spectrum of the β-rays emitted from tritium atoms is shown in Fig. 1. No electromagnetic radiation comes from nucleus. Although penetration power of the β-rays is very weak, a part of kinetic energy of β-rays is

Table 2. Summary of half-life of tritium nuclei.

| Year | Half-life, Years | References |
|---|---|---|
| 1940 | 0.41±0.11 | L.W. Alvarez and R. Comog, Radioactive hydrogen Phys. Rev.., **57** (1940) 248. |
| 1940 | >10 | L.W. Alvarez and R. Comog, Phys. Rev., **58** (1940) 197. |
| 1940 | 31±8 | R.D. O'Neal and M. Goldhaber, Phys. Rev., **58** (1940) 574. |
| 1947 | 12.1±0.5 | A. Novick, Phys. Rev., **72** (1947) 972. |
| 1947 | 10.7±2.0 | M. Goldblatt, E.S. Robinson and R.W. Spence, Phys. Rev., **72** (1947)973. |
| 1949 | 12.46±0.2 | G.H. Jenks, J.A. Ghormley and F.H. Sweeton, Phys. Rev., **75** (1949) 701. |
| 1950 | 12.46±0.1 | G.H. Jenks, F.H. Sweeton and J.A. Ghormley, Phys. Rev., **80** (1950) 990. |
| 1951 | 12.41±0.04 | W.M. Jones, Phys. Rev., **83** (1951) 537. |
| 1955 | 12.262±0.004 | W.M. Jones, Phys. Rev., **100** (1955) 124. |
| 1958 | 12.58±0.18 | M.M. Povov, I. V. Gagarinskii, M.D. Senin, I.P. Mikhalenko and I.M. Morozov, Atomnaya Energiya, **4** (1958) 296. |
| 1963 | 12.355±0.010 | J.F. Eichelberger, G.R. Grove and L.V. Jones, USAEC Report MLM-1160, Mound Laboratory, (1963). |
| 1963 | 12.355±0.010 | J.F. Eichelberger, G.R. Grove and L.V. Jones, USAEC Report MLM-1176, Mound Laboratory, (1963). |
| 1966 | 12.31±0.13 | J.S. Merritt and J.G.V. Taylor, Report AECL-2510, Chalk River Lab., 1966. |
| 1967 | 12.346±0.002 | K.C. Jordan, B.C. Blanke and W.A. Dudley, J. Inorg. Nucl. Chem., **29** (1967) 2129. |
| 1967 | 12.25±0.08 | P.M.S. Jones, J. Nucl. Mater., **21** (1967) 239. |
| 1977 | 12.323±0.004 | C.R. Rudy and K.C. Jordan, Progress Report MLM-2458, US DOE, Mound Lab., 1977 |
| 1980 | 12.43±0.05 | M.P. Unterweger B.M. Coursey, F.J. Schima, and W.B. Mann, Int. J. Appl. Radiat. Isot., **31** (1980) 611. |
| 1987 | 12.29±0.10 | B. Budic and H. Lin, Bull. Am. Phys. Soc., **32** (1987) 1063. |
| 1987 | 12.38±0.03 | B.M. Oliver, H. Farrar IV and M.M. Bretscher, Appl. Radiat. Isot., **38** (1987) 959. |
| 1987 | 12.32±0.03 | J.J. Simpson, Phys. Rev. C, **35** (1987) 752. |
| 1988 | 12.279±0.033 | Y.A. Akulov, B.A. Mamyrin, L.V. Khabarin, V.S. Yudenich and N.N. Ryazantseva, Pis'ma Zh. Tekh. Fiz.,**14** (1988) 940. |
| 1991 | 12.31±0.03 | B. Budic, J. Chen and H. Lin, Phys. Rev. Lett., **67** (1991) 2630. |
| 2000 | 12.33±0.03 | M.P. Unterweger and L.L. Lucas, Appl. Radiat. Isot., **52** (2000) 527. |
| 2000 | 12.32±0.02 (4500±8 days) | L.L. Lucas and M.P. Unterweger, J. Res. Natl. Inst.Stand. Technol., **105** (2000) 541. |
| 2004 | 12.264±0.018 | Yu.A. Akulov and B.A. Mamyrin, Phys. Letters B, **600** (2004) 41. |
| 2006 | 12.31±0.01 (4497±4 days) | Desmond MacMahon, Appl. Radiat. Isot., **64** (2006) 1417. |

converted into electromagnetic radiations such as characteristic and/or bremsstrahlung X-rays when the β-rays plow through the nearby matter. Since the penetration power of these X-rays is much stronger than that of the β-rays, they can be used as a probe of tritium detection as described later.

The half-life of tritium nuclei is one of very important physical constants, and it has been examined by many researchers since discovery of tritium as shown in Table 2 [1]. Several methods have been applied to determine the half-life of tritium nuclei. Measurements of changes in the radioactivity of tritium by an ionization chamber and a proportional counter were applied to determination of the half-life. In addition, calorimetric method and $^{3}He$ measurement had been also applied to this purpose. At the present time, most reliable half-life of tritium nuclei is 4500±8 days (12.32±0.02 years). However, if the present half-life is applied to the amount of tritium in a fusion reactor, a fairly large amount of tritium shall be unknown after a long period. For example, when initial loading amount of tritium is 10,000 g, it decreases to 5697±5 g after 10 years by decay only. Namely, uncertainty of the amount of tritium will reach to ±5 g.

## III. Main Fuel Circulation System in a Fusion Reactor and Related Technologies

A fuel circulation system is indispensable to operate continuously a fusion reactor by supplying and recovering fuel particles. Schematic diagram of the fuel circulation system is shown in Fig. 2. As for basic handling technologies for high-level tritium in fusion environment, there are five major technologies: namely, (1) basic technologies for supply, recovery, purification, separation and storage in a main fuel circulation system, (2) breeding and recovering technologies of tritium in/from the blanket system, (3) enclosing technologies by multi-enclosure and establishment of high permeation barrier, (4) decontamination technologies for various contaminated materials and for liquid waste

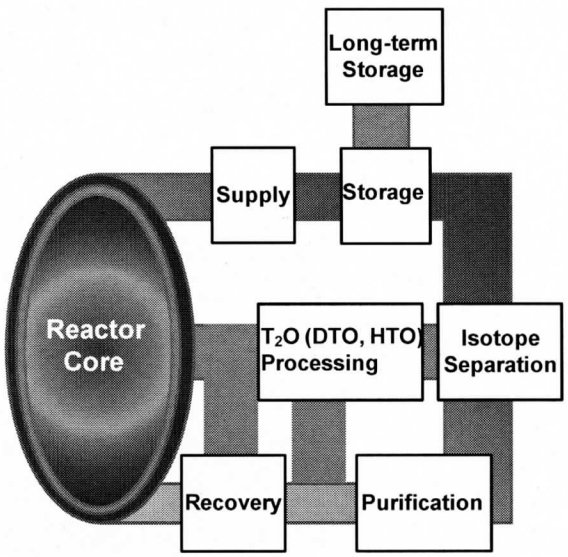


Fig. 2 Schematic diagram of the fuel circulation system for fusion reactor.

such as tritiated water, and (5) common technologies related with tritium measuring techniques for measurement of tritium partial pressure (or concentration), analyses of chemical form of tritium species, estimation of a partial inventory in a sub-system of the fueling system, and so on.

To satisfy the fifth technology mentioned above, a variety of devices and techniques must be provided in advance to analyze tritium species in various physical and chemical states as shown later. Most

important functions of these devices are high reliability and durability over a long period.

## IV. Techniques for Tritium Measurements

It is necessary to measure tritium concentration in a remarkably wide range from environmental level to fusion fuel level as shown in Fig. 3. In addition to the range of tritium concentration, not only elemental tritium but also different chemical form of tritium species such as oxidized tritium and tritiated hydrocarbon increase with the operation time of a fusion reactor. To evaluate such tritium concentration, most suitable device for each tritium species will have to be prepared.

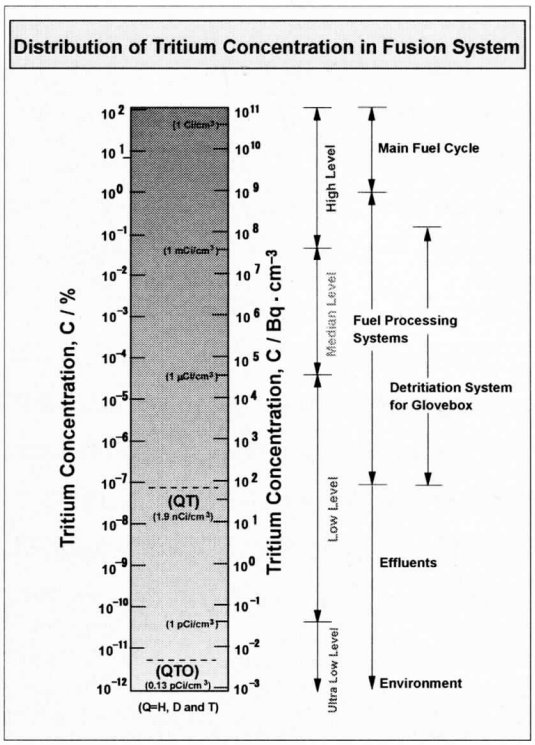


Fig. 3 Tritium concentration in fusion environment.

Various devices have been developed so far for tritium measurements as shown in Table 3. Upper three methods in the table are categorized as an absolute measurement method. The others are relative measurement methods and widely used for tritium measurements. In addition to these methods and devices, some techniques are applicable: for example, imaging plate (IP), autoradiography, window-less G-M counter, electret dosimeter, and β-ray-induced X-ray spectrometer (BIXS). The last one is a new method that was recently developed by Matsuyama et al. as a nondestructive measuring method [2]. An example applied this technique will be described in the next session.

Table 3. List of the measuring devices for tritium.

| Method / Device | Common Working Range | physical state | | | Real-time Measurement | Remark |
|---|---|---|---|---|---|---|
| | | gas | liquid | solid | | |
| Volumetry | ~ above 370 MBq | ○ | --- | --- | --- | requirement of purity data |
| Gravimetry | ~ above 3.7 GBq | --- | △ | △ | --- | requirement of purity data |
| Calorimeter | ~ above 3.7 GBq | ○ | ○ | ○ | --- | large amount of tritium |
| Mass Spectrometer | ~ below 10-3 Pa | ○ | --- | --- | △ | processing of exhaust gases |
| Gas Chromatography | ~ below 37 GBq | ○ | --- | --- | --- | processing of effluent gases |
| Infrared Absorp. Spectrom. | ~ above 1 Pa | --- | ○ | △ | △ | stability of infrared beam intensity |
| Laser Raman Spectrometer | ~ above 100 Pa | ○ | --- | △ | △ | stability of laser beam intensity |
| Electron Multiplier | ~ below 10-3 Pa | ○ | --- | △ | △ | processing of exhaust gases |
| Ionization Chamber | 37 mBq/cm$^3$ - carrier free | ○ | --- | --- | △ | depending on chamber volume |
| Proportional Counter | ~ below 370 kBq | ○ | --- | △ | △ | requirement of quenching gas |
| Inorg. Scinti. Counter | ~ above 10 kPa | ○ | --- | --- | △ | contamination of scintillator |
| Liquid Scintillation Counter | ~ below 370 kBq | --- | ○ | △ | --- | processing of liquid waste |
| Plastic Scintillation Counter | ~ below 370 kBq | --- | ○ | △ | △ | contamination of scintillator |

## V. New Device for In-Situ Measurement of Highly Tritiated Water

Generation of highly tritiated water is inevitable in the fuel circulation system and tritium breeding blanket system of a fusion reactor. It is well known that a liquid scintillation counter (LSC) is widely used for determination of tritium concentration in the water. Measurements by a conventional LSC, however, are limited below about a few hundred kBq/cm$^3$ due to saturation of a photo-multiplier. To measure highly tritiated water above this level it is required to dilute the tritiated water with normal water up to the suitable tritium concentration. This process is dangerous procedures as well as enlargement of error. Therefore, development of a new device which is able to measure in-situ highly tritiated water had been desired.

Figure 4 shows a schematic diagram of a new device, which is based on the method of BIXS mentioned above. A part of energy of β-rays emitted in the tritiated water is converted into bremsstrahlung and characteristic X-rays in the water. These X-rays penetrate through a thin beryllium window, and enter the specially designed X-ray detector. The beryllium surface contacting with water was covered with a thin gold film to avoid the erosion of beryllium surface. The present device is applicable to not only a batch system but also a flow system of tritiated water. Figure 5 describes the calibration curve prepared by using the conventional LSC which was previously calibrated using the standard tritiated water. As seen clearly from the

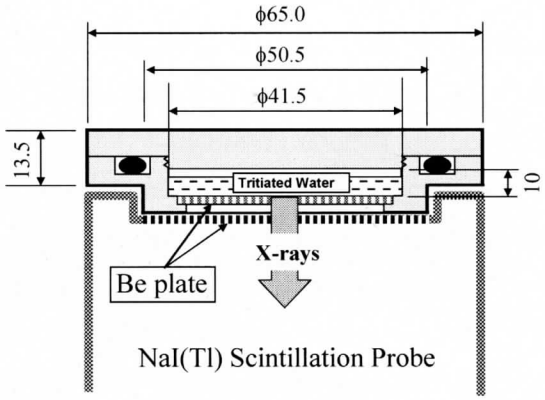


Fig. 4 A cross-sectional view of a new device to measure highly tritiated water.

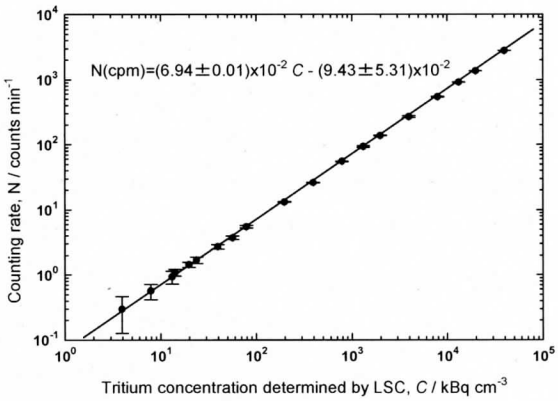


Fig. 5 Calibration curve of the new device for highly tritiated water.

figure, a good linear relation appears in a higher region than 4 kBq/cm$^3$ of tritium concentration [3].

## VI. Material Dependence of Tritium Inventory

A serious problem is still remained in the development of a detector for high-level elemental tritium. When a tritium detector is exposed to elemental tritium, a part of the tritium gas adsorbs on the surface and then it dissolves into the bulk through surface layers. A background level of the detector becomes high owing to the residence of tritium on the surface and in surface layers of detector materials, which is so-called memory effect. This phenomenon disturbs

precise measurements and gives rise to increase in the lower detection limit. It is indispensable to research and develop new functional materials available to the atmosphere of high-level tritium.

Figure 6 shows the solubility of tritium in fusion reactor materials [4]. Both of endothermic and exothermic reactions with tritium are described in the figure. As seen clearly from the figure, solubility of tritium in W, Al, Mo and Cu at lower temperatures is less than that in stainless steel which is widely used as a structural material in fusion related devices. Although these materials are advantageous for tritium handling devices on account of low solubility, it is hard to machine W and Mo materials owing to low ductility and high hardness. On the other hand, Al and Cu materials are disadvantageous because of lack of mechanical properties. However, it is possible to make up weak points by alloying and surface modification of these materials. For example, hardness of Cu-Be alloys is almost same as that of stainless steel, and surface hardness of Al can be improved by surface coating with a thin TiN film.

It is known that the tritium concentration in surface layers of stainless steels is remarkably enriched in comparison with that in the bulk [5]. Surface concentration of tritium gradually increased again by diffusion from the bulk, if tritium atoms trapped in the surface layers could be removed by a special decontamination method. Namely, it is very important to reduce the tritium concentration in the bulk as well as the surface. From this viewpoint,

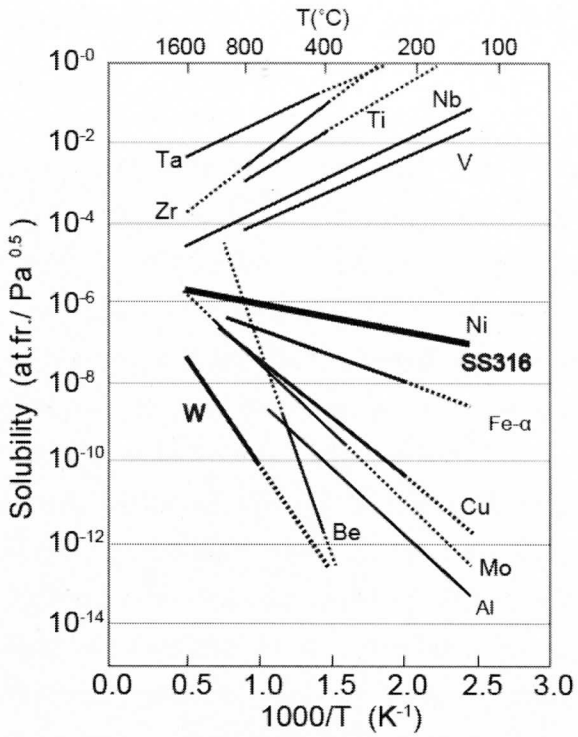


Fig. 6 Solubility of tritium in various materials.

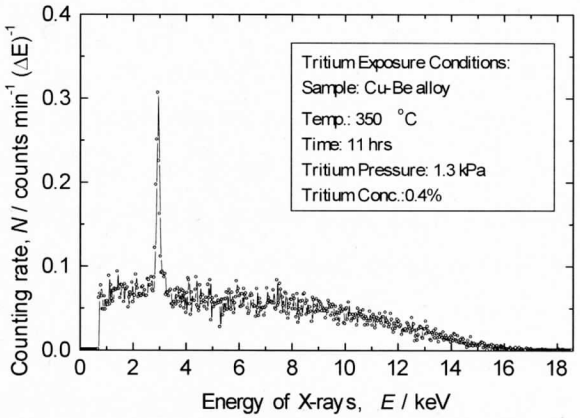


Fig. 7 X-ray spectrum induced by β-rays emitted from tritium.

solubility of tritium in Cu-Be(2 mass %) alloy was examined at low temperatures.

Figure 7 describes an example of X-ray spectra measured by β-ray-induced X-ray spectrometry (BIXS), after the Cu-Be alloy samples were exposed to tritium gas at 623K for 11 hours. The total pressure of tritium gas was 1.3 kPa, and the tritium concentration was 0.4%. The details of

BIXS are shown in elsewhere [6]. A sharp and intense peak is the characteristic X-ray peak of Ar, which is mainly induced by tritium adsorbed on the surface. On the other hand, broad and weak peak is the bremsstrahlung X-rays, which is caused by the interactions between β-rays and constituent atoms of the sample. The shape of this peak depends on a depth profile of tritium in the bulk. The observed spectrum indicates that a large fraction of tritium is relatively trapped on the surface and in surface layers in comparison with the bulk.

Figure 8 shows the tritium depth profile measured by a chemical etching method after measurement of the X-ray spectrum mentioned above. Although high tritium concentration appeared in surface layers within a few μm as suggested from analyses of the X-ray spectrum, tritium concentration in the bulk was almost constant as $2.7 \times 10^4$ Bq/cm$^3$, which corresponds to $3.8 \times 10^{15}$ atoms/cm$^3$. The number of metallic atoms in Cu-Be alloy is $8.76 \times 10^{22}$ atoms/cm$^3$, which was evaluated using lattice constant of the alloy estimated from an X-ray diffraction pattern. Atomic fraction of tritium in alloy was as low as $4.33 \times 10^{-8}$. From this atomic fraction, solubility of tritium at 623K was estimated as $1.2 \times 10^{-9}$ at.fr./Pa$^{0.5}$, considering the total pressure of tritium gas. It was seen, therefore, that the solubility of tritium in Cu-Be alloy was below around 1/400 in comparison with that in SS316 described in Fig. 6. The result indicates that Cu-Be alloy is one of promising materials for tritium handling devices. However, more studies will be required to improve surface properties of the Cu-Be alloys.

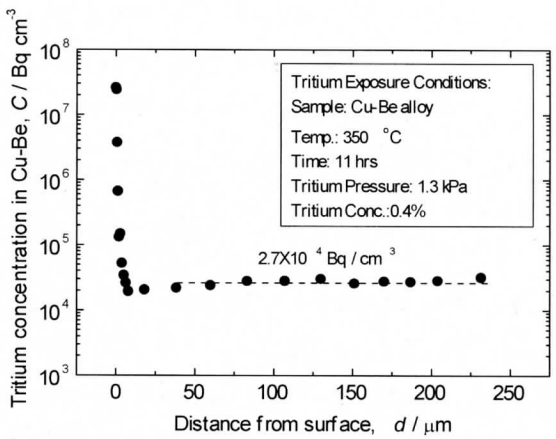


Fig. 8 Depth profile of tritium in Cu-Be alloy.

## VII. Important Issues toward Future Fusion Reactors

Safe and precise control of a huge amount of tritium will be required for a future fusion reactor. Additionally, it is not clear whether the present measuring devices are durable enough for a continuously long run. For these reasons it is necessary to improve the existing methods and techniques and to develop new measuring methods and techniques applicable to a fusion reactor. Therefore, the following issues must be examined to establish the tritium plant in the fusion reactor.

[1] Improvement of existing methods and techniques:

(1) Reduction of memory effects: to reduce the amount of tritium adsorbed on the surface and that absorbed in surface layers of the detector materials.

(2) Increase in durability: to be long-life and maintenance free (or easy maintenance)

(3) Increase in sensitivity: to extend a working range, especially improving lower detection limit.

(4) Increase in precision and accuracy: to increase in stability of the detectors.

(5) Compactness and simplification: to lower tritium inventory and trouble frequency.

[2] Development of new measuring methods and techniques:

Various kinds of chemical form and physical state of tritium exist in the fusion system. In addition to this, many kinds of radioactive nucleus produced by neutron irradiations also coexist in the fusion system. The best method should be applied to each system and purpose. Various methods and technique have to be provided from viewpoint of precise control and evaluation of high-level tritium.

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