The Series of Environmental Radioactivity Measuring Methods

AN-H3
(No.9)

Tritium Analysis

Amendment of October 2023
Radiation Monitoring Division
Radiation Protection Department
The Secretariat of
Nuclear Regulation Authority

NRA JAPAN
Nuclear Regulation Authority

This document was written in Japanese and translated into English.
The Japanese version is the original and the English version was written as a reference.

Table of Contents

Chapter 1 Introduction ····· 1
Chapter 2 Water samples ····· 5
2.1 Sampling ····· 5
2.1.1 Sampling location and frequency ····· 5
2.1.2 Precautions for sample collection ····· 5
2.2 Purification of sample water ····· 6
2.2.1 Atmospheric distillation ····· 6
2.2.2 Vacuum distillation ····· 7
2.3 Electrolytic enrichment of tritium ····· 12
2.3.1 Electrolytic enrichment with metal electrodes ····· 13
2.3.2 Electrolytic enrichment with solid polymer electrolyte (SPE) ····· 21
Chapter 3 Atmospheric Samples ····· 25
3.1 Sampling ····· 26
3.1.1 Sampling location and frequency ····· 26
3.1.2 Precautions for sample collection ····· 26
3.2 Sampling methods ····· 28
3.2.1 Methods using molecular sieves ····· 28
3.2.2 Methods using silica gel ····· 31
3.2.3 Methods using a dehumidifier ····· 33
3.2.4 Passive method ····· 34
3.3 Purification of sample water ····· 36
3.3.1 Atmospheric distillation ····· 36
3.3.2 Vacuum distillation ····· 36
Chapter 4 Biological Samples ····· 46
4.1 Sampling ····· 46
4.1.1 Sampling location and frequency ····· 46
4.1.2 Precautions for sample collection ····· 46
4.2 Recovery of tissue-free water by the vacuum freeze-drying method ····· 48
4.3 Recovery of combustion-generated water ····· 49
4.3.1 Combustion method ····· 49
4.3.2 Rapid combustion method ····· 52
4.4 Purification of sample water ····· 55
4.4.1 Wet decomposition (reflux) ····· 55
4.4.2 Distillation of refluxed sample ····· 56
Chapter 5 Setting and Calibration of Measurement Conditions ····· 60
5.1 Preparation of standard samples for quenching-correction curve ····· 60
5.1.1 Preparation method ····· 60
5.2 Background sample preparation ····· 61
5.3 Setting of measurement conditions ····· 64

5.3.1 Setting the measurement conditions based on the figure of merit (FOM) ····· 64
5.3.2 Setting the measurement conditions for determining the quenching index value using external standard sources ····· 68
5.4 Calibration: Preparation of quenching-correction curves ····· 70
Chapter 6 Measurement ····· 72
6.1 Preparation of measurement samples ····· 72
6.2 Measurement ····· 76
6.2.1 Sample measurement ····· 76
6.2.2 Precautions for measurement ····· 76
6.2.3 Data rejection test ····· 77
6.2.4 Calculation of radioactivity concentration ····· 78
6.2.5 Uncertainty ····· 82
6.2.6 Lower detection limit ····· 82
Chapter 7 Quality Assurance ····· 84
7.1 Internal quality control ····· 84
7.1.1 Ensuring traceability ····· 84
7.1.2 Daily inspection ····· 84
7.2 External quality control ····· 86
7.2.1 Interlaboratory comparison ····· 86
7.2.2 Proficiency test ····· 86
Explanation ····· 87
Explanation A Electrolytic Enrichment of Tritium ····· 89
Explanation B Calculation of Absolute Humidity ····· 94
Explanation C Study on the Vacuum Freeze Drying of Biological Samples ····· 96
Explanation D Results of Investigation and Review of Commercial Emulsified Scintillators and Measuring Containers ····· 98
Explanation E Data Rejection Test ····· 104
Explanation F Example of Radioactivity Concentration Calculation ····· 110
Explanation G Evaluation of Uncertainty in Tritium Analysis ····· 115
Explanation H Calculation example of the lower detection limit ····· 129
Information ····· 145
Information A Study of purification method for water samples using ion-exchange resins ····· 147
Information B Collecting tritium from the atmosphere using bubbling and condensation methods 151
Information C Analysis procedure for nonexchangeable OBT ····· 155
Information D Quantification of tritium via ^{3}He mass spectrometry ····· 163
Appendix ····· 165
Appendix A Nuclear Data for Tritium ····· 167
Appendix B Explanation of Terms ····· 168
Appendix C Analysis Flow ····· 170
References ····· 173

Chapter 1 Introduction

Tritium is a pure β-ray-emitting nuclide with a half life of 12.32 years and a maximum β-ray energy of 18.6 keV[1]. Its sources[2] can be broadly divided into two categories: natural sources and artificial sources. Natural sources refer to those which produce tritium through nuclear reactions between secondary cosmic rays generated from primary cosmic rays and nitrogen or oxygen in the upper atmosphere (e.g., $^{14}N + n \rightarrow {}^{3}H + {}^{12}C$), and artificial sources are those which emit tritium into the environment during atmospheric nuclear tests or from nuclear facilities (nuclear power plants and reprocessing facilities). Furthermore, tritium is produced during the spontaneous nuclear fission of uranium and other substances in the Earth's crust and from lithium; however, the amount of tritium produced in these manners is negligible compared with that produced in the atmosphere[2,3]. The amount of tritium produced annually in the atmosphere is estimated to be 72 PBq (P (peta) = 10^{15})[4]. Most of it is oxidized into tritiated water (HTO: one hydrogen atom replaced by tritium (T)) and incorporated into the water cycle as atmospheric moisture, rain water, land water, seawater, etc[5]. Other than HTO, the chemical forms of tritium include gaseous tritium (HT, CH_3T); tissue-free water tritium (TFWT), in which tritium is incorporated into biological samples; and organically bound tritium (OBT). Furthermore, OBT can be classified into two types: exchangeable type, in which tritium is bound to oxygen or nitrogen atoms and is easily exchanged with hydrogen, and nonexchangeable type, in which tritium is bound to carbon chains and cannot be easily exchanged.

Because tritium is an isotope of hydrogen, a major constituent element of the human body, upon ingestion, the chemical form of tritium, which has different metabolic behaviors[6], is important for evaluating the exposure dose. When tritium enters the body through three routes—respiration (inhalation), skin (absorption), and food and drink (ingestion)—the chemical forms to be considered are atmospheric moisture and hydrogen gas in the respiration and skin routes and water and tritium in the organic form in the food and drink, respectively. Knowledge regarding the behavior of tritium in environmental ecosystems, including agricultural, livestock, and fishery products, is also required.

The first edition of this book describing an analytical method for tritium concentration estimation was published in 1977 as a tritium analysis method for environmental monitoring around nuclear power plants, nuclear fuel reprocessing plants, and other nuclear facilities. Its revised second edition was established in 2002, with detailed analysis methods for atmospheric and biological samples as well as additional content related to technological advances.

Nearly 20 years have passed since the publication of the second edition. During that time, the accident at the Fukushima Daiichi Nuclear Power Plant of Tokyo Electric Power Company (TEPCO) in the wake

---

[1] Evaluated Nuclear Structure Data File (ENSDF)

[2] 宇田達彦, 田中将裕: 小特集 施設起源トリチウムの移行モデルと環境トリチウム分布. 2.環境トリチウムの現状と分布. 2.1 大気中トリチウム濃度の変遷と化学形態別測定, *J. Plasma Fusion Res.*, **85(7)**, 423-425 (2009).

[3] Institute de Radioprotection et de Sûreté Nucléaire (IRSN) (French institute for radiation protection and nuclear safety); Radionuclide sheet: Tritium and the environment (2010).

[4] United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). *Sources and Effects of Ionizing Radiation*, UNSCEAR 2000 Report to the General Assembly, with Scientific Annexes, Volume I: Sources, Annex A: Dose assessment methodologies (2000).

[5] 柿内秀樹: 小特集 トリチウム分離・濃縮技術. 4.環境分析のためのトリチウム電解濃縮, *J. Plasma Fusion Res.*,**92(1)**,26-30(2016).

[6] UNSCEAR. (2016). *Sources, Effects and Risks of Ionizing Radiation.* UNSCEAR 2016 Report to the General Assembly, with Scientific Annexes, Annex C: Biological effects of selected internal emitters - Tritium.

of the Great East Japan Earthquake occurred (hereinafter referred to as 1F accident) and a large amount of artificial radionuclide was released into the environment. To treat contaminated water with artificial radionuclides generated by the 1F accident, a multinuclide removal system (Advanced Liquid Process System or ALPS) is being used to remove 62 nuclides including radioactive cesium.[7] However, because tritium cannot be removed using the ALPS, the amount of ALPS treated water (water that has been purified by utilizing the ALPS to meet the regulatory standards for other radionuclides than tritium) containing tritium has been increasing annually. In 2021, the Cabinet approved the discharge of the ALPS treated water into the ocean, and interest in tritium has been growing.

Under these circumstances[8], assurance regarding the reliability of analytical capabilities through interlaboratory comparison (hereinafter referred to as ILC) among analytical laboratories and maximum objectivity and transparency is required for tritium analysis and its analytical results, as stated in the Basic Policy for Disposal of ALPS Treated Water. Meanwhile, the measurement of the tritium concentration in environmental samples around nuclear facilities is also required, as mentioned in the NRA Guideline for Emergency Preparedness and Response[9] and their supplementary reference materials[10] established after the 1F accident.

Based on the above, a description regarding the uncertainty required for proficiency tests[11] such as ILC among analytical laboratories, the calculation of the low detection limit (hereinafter referred to as DL) based on ISO 11929[12], which is considered common outside Japan, and these topics are added in this revision. Note that because the excretion rate of non-exchangeable OBT differs from that of the other chemical forms of tritium and may be evaluated separately in dosimetry, the crosscheck results along with their analytical methods are included as reference materials. In addition, the flow of the analysis method is summarized in the Appendix to provide the workflow and their overall view. Although this analytical method focuses on tritium analytical methods in environmental samples under normal conditions, a wide range of related information and literature are included for reference so that the method can be applied to analysis for other purposes such as rapid one.

Although not limited to tritium analysis, selecting an appropriate method depending on the purpose of analysis and measurement is necessary. For example, to investigate changes in the tritium concentration over time, an analytical method with a low DL may be selected to realize a quantitative analysis with high accuracy, although this analysis is time-consuming. For environmental samples that are at background levels when monitoring tritium under normal conditions, if the objective is to confirm

---

[7] Ministry of Economy, Trade and Industry (METI). Disposal of ALPS Treated Water. https://www.meti.go.jp/earthquake/nuclear/hairo_osensui/alps.html

[8] The Cabinet Meeting on Contaminated Water, Treated Water and Reactor Decommissioning issues. (2021). *Basic Policy for handling of ALPS Treated Water at the TEPCO's Fukushima Daiichi Nuclear Power Station*. https://www.meti.go.jp/earthquake/nuclear/hairo_osensui/alps_policy.pdf

[9] The Nuclear Regulation Authority. NRA Guideline for Emergency Preparedness and Response (Partially amended on July 6, 2022)

[10] Radiation Monitoring Division, the Secretariat of the Nuclear Regulation Authority, Ordinary Monitoring (Supplementary Reference Materials for The Guideline for Emergency Preparedness and Response) (Revised December 21, 2021)

[11] JIS Q 17043: 2011, "Conformity Assessment - General Requirements for the Proficiency Testing" defines proficiency testing as the evaluation of a participant's performance against predetermined criteria through inter-laboratory comparison.

[12] International Organization for Standardization. (2022). ISO 11929-4:2022. Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation - Fundamentals and application. Part 4: Guidelines to applications.

that they are below the target lower DL, an analytical method that can achieve this limit shall be selected. Furthermore, if a large number of samples are to be screened and analyzed to confirm quickly that they are below the target low DL, a method that meets this limit and has the shortest possible analysis time shall be selected. This analytical method does not blindly require highly accurate analysis and measurement, nor does it deny the more reliable and appropriate methods that have been developed as new technologies are being researched constantly. It only requires a reasonable selection of necessary methods to achieve objectives and describes necessary procedures technically necessary to achieve objectives.

To assist in method selection, detectable levels obtained from several combinations of analytical and measurement methods are shown below for reference.

Table 1.1 Detectable tritium levels in water samples

Measurement container	Measurement time (min)	Detectable level (Bq/L) *1 – *3	
		Distillation process	Electrolytic enrichment method*4
20 mL glass vial	100	10	2
	500	5	0.8
	1000	3	0.6
20 mL polyethylene vial	100	4	0.6
	500	2	0.3
	1000	1	0.2
100 mL fluoroplastic vial	100	1	0.2
	500	0.5	0.08
	1000	0.3	0.05
145 mL polyethylene vial	100	0.7	0.1
	500	0.3	0.05
	1000	0.2	0.04

*1 The mixing ratio of the water sample and emulsified scintillator shall be 1:1.

*2 The counting efficiency of the liquid scintillation counter shall be 25%.

*3 The background counting rate for each container shall be 20 cpm (counts per minute) for a 20 mL glass vial, 2 cpm for a 20 mL polyethylene vial, and 4 cpm for a 100 mL fluoroplastic vial and a 145 mL polyethylene vial, respectively.

*4 The tritium concentration ratio for electrolytic enrichment (Ni–Ni electrode) shall be 6.

Table 1.2 Detectable tritium levels in atmospheric samples

Subject	Atmospheric intake volume (m^3)	Measurement time (min)	Detectable level (mBq/m^3) *1 – *3
Tritiated water (HTO)*4	10	100	20
		500	7
		1000	5
Hydrogen–tritium (HT)*5	10	100	9
		500	4
		1000	3

*1 The measurement container shall be a 100 mL fluoroplastic vial, and the mixing ratio of the emulsified scintillator to the collected water sample shall be 1:1.

*2 The counting efficiency of the liquid scintillation counter shall be 25%.

*3 The background counting rate for a 100 mL fluoropolymer vial shall be 4 cpm.

*4 Temperature, relative humidity, and absolute humidity shall be 25°C, 70%, 16 g/m^3, respectively.

*5 The collection volume shall be 80 g including tritium-free hydrogen-gas carrier, and the oxidation efficiency shall be 90 %.

Table 1.3 Detectable tritium levels in biological samples

Subject	Measurement time (min)	Detectable level (Bq/L) *1– *3	Detectable level (Bq/kg of raw mass) *1 – *4
Tissue-free water tritium (TFWT)	100	1	0.8
	500	0.5	0.3
	1000	0.3	0.2
Organically bound tritium (OBT)	100	1	0.1
	500	0.5	0.06
	1000	0.3	0.04

*1 The measurement container shall be a 100 mL fluoroplastic vial, and the mixing ratio of the emulsified scintillator to the collected water sample shall be 1:1.

*2 The counting efficiency of the liquid scintillation counter shall be 25%.

*3 The background counting rate for a 100 mL fluoropolymer vial shall be 4 cpm.

*4 The combustion sample weight, recovered water content, and moisture percentage shall be 140 g, 75 mL, and 75%, respectively.

Chapter 2 Water samples

Water samples include land water (rivers, lakes, and ponds), drinking water (city water, tap water, and ground water), seawater, and precipitation. Water should be purified via distillation to obtain the sample for measurement.

2.1 Sampling

For details regarding the method used for collecting water samples, refer to the Radioactivity Measurement Methods Series No. 16 “Method for sampling of Environmental Materials" and No. 35 "Generic Procedures for Environmental Sampling in Emergencies".

2.1.1 Sampling location and frequency[13]

(1) Sampling location

As a general rule, sampling locations shall be determined according to the purpose of the measurement. When determining sampling locations from the perspective of environmental monitoring around nuclear facilities, it is desirable to consider the environmental conditions around the facility. In this case, it is particularly important to remember to collect raw drinking water supplied in the vicinity of the facilities. In addition, setting comparison points that can serve as background data will be helpful when evaluating data.

(2) Sampling frequency

Samples shall be collected 2–4 times per year from land water, drinking water, and seawater. However, if raw drinking water is likely to be contaminated by tritium, sampling shall be done once a month. Precipitation is collected after each rainfall, and a month’s worth of precipitation is used as a sample for measurement.

2.1.2 Precautions for sample collection

(1) Sample volume

The sample volume shall be approximately 0.5–2 L, considering the analysis method, loss in the analysis process, storage for repeated analysis, etc. If electrolytic enrichment is performed, approximately 2 L is required.

(2) Sample processing method

If necessary, remove suspended solids from collected samples via sedimentation or filtration (filter paper No. 5C). Furthermore, do not add acid.

(3) Sample storage

The collected sample is preferably stored in a tightly closed sample container (glass bottle, plastic container[14], etc.) to prevent evaporation and contamination by atmospheric water vapor.

---

[13] This description is an example. When establishing the monitoring plan, refer to the NRA Guideline for Emergency Preparedness and Response and its Supplementary Reference Materials "Ordinary Monitoring" and "Emergency Monitoring. ”

[14] At sites where tritium sources are handled or where tritium is generated by nuclear reactions, tritium shall be stored in plastic containers with a sufficient degree of sealing equivalent to glass containers to prevent contamination by atmospheric vapor with high tritium concentration.

(4) Sample records

Refer to Radioactivity Measurement Methods Series No. 16 "Method for sampling of Environmental Materials" and No. 35 "Generic Procedures for Environmental Sampling in Emergencies."

(5) Measures to prevent sample contamination

There are reports that sample water was contaminated by tritium leaking from a foreign-made radioluminous watch[15], hence, caution is needed. In addition, tritium concentrations in environmental samples are extremely low, while samples from the working environment in nuclear facilities are common that have high tritium concentrations. Therefore, when samples with extremely different levels coexist, it is advisable to take measures such as storing them in sealed containers and separating storage areas to prevent the contamination of low-concentration samples.

2.2 Purification of sample water

To accurately determine low-level tritium concentrations, it is necessary to remove radionuclides other than tritium, salts, etc. Generally, atmospheric and vacuum distillation methods are used to purify samples. Vacuum distillation is faster than atmospheric one: approximately 1 h is needed to distill 100 mL water sample by vacuum distillation and 5–6 h is required in the case of atmospheric distillation.

The purpose of performing distillation is as follows.

- Perform desalination treatment to minimize interference during measurement
- Separate from radionuclides other than tritium
- Separate from foreign organic matter

Distillation is also required before and after electrolytic enrichment as described in 2.3.1 Electrolytic Enrichment with Metal Electrodes. In addition to the above, the purpose of conducting distillation before electrolysis is to perform desalting to maintain electrolytic conditions constantly between samples, and the purpose of distillation after electrolysis is to remove added electrolytes.

2.2.1 Atmospheric distillation

The following laboratory equipment and reagents are required for atmospheric distillation. Figure 2.1 shows the schematic of a distillation unit.

(1) Laboratory equipment

- Eggplant-shaped flask (100 mL)
- Distillate (distilled water in this case) collector (with faucet and 100 mL scale)
- Cooling tube (Liebig type)
- Connector
- Mantle heater (100 W)
- Voltage regulator (not required if built into the mantle heater)
- Conductivity meter

(2) Reagents

[15] 徳山秀樹, 吉田暁美: 夜光時計から漏洩した水蒸気状トリチウムの水への移行, *RADIOISOTOPES*, **47**,560-562(1998).

- Sodium peroxide (Na_2O_2): granular (purity ≥95%)
- Potassium permanganate ($KMnO_4$): JIS special grade reagent
- Silver nitrate ($AgNO_3$) solution: Dissolve 1 g silver nitrate in 100 mL 0.1 mol/L nitric acid.
- Conductivity standard solution (~140 mS/m)
- Boiling stones
- Silica gel

(3) Procedure

1) Take the sample water[16] in an eggplant-shaped flask[17], add sodium peroxide and potassium permanganate at approximately 0.1 w/w% of the sample volume[18], and dissolve them in the water. Add a small number of boiling stones to prevent vigorous boiling. Note that glassware shall be thoroughly dried before use.
2) Assemble the distillation apparatus, ensure the flow of cooling water, switch ON the mantle heater, and gradually increase the temperature.
3) The distilled water is collected in the eggplant-shaped flask, and distillation is continued until the sample is dry[19]. Take care to prevent the vigorous boiling of the sample[20].
4) Pour a few milliliters of the obtained distilled water into a beaker[21], add the silver nitrate solution into it in a drop-wise manner, and check whether or not a white precipitate (silver halide such as AgCl) is formed. If the water becomes cloudy, distill the obtained distilled water again. Alternatively, measure electrical conductivity using the electrical conductivity meter and confirm that conductivity is approximately 1 mS/m or less equivalent to the electrical conductivity of purified water produced by a commercially available water purifying apparatus).
5) The obtained distilled water should be used immediately to prepare the measurement sample or, if time is required, store it in a tightly sealed sample container (glass bottle, plastic container[22], etc.)[23].

2.2.2 Vacuum distillation

The following laboratory equipment and reagents are required for vacuum distillation method. Figure 2.2 shows the schematic of the distillation apparatus.

(1) Laboratory equipment

- Eggplant-shaped flask (1 L)
- Round-bottom flask (1 L)
- Cylindrical distillation tube

[16] The sample water amount is determined by considering the volume required for the measurement sample.

[17] Glassware such as flasks shall be thoroughly dried before use. Not only in this case, but in any tritium analysis, moisture can cause contamination; therefore, ensure that all equipment used are thoroughly dried.

[18] Sodium peroxide and potassium permanganate should be added at approximately 0.1 w/w% of the sample volume to decompose organic matter in the sample water. If there is no interference from organic matter or salts in the sample water, adding these reagents is not necessary.

[19] Because H_2O and HTO have different boiling points, ensure to collect each completely.

[20] If bubbles begin to form violently, reduce the voltage of the mantle heater to prevent vigorous boiling.

[21] Take care not to let condensed water get into the sample.

[22] At sites where tritium sources are handled or where tritium is generated by nuclear reactions, tritium shall be stored in plastic containers with a sufficient degree of sealing equivalent to glass containers to prevent contamination by atmospheric vapor with high tritium concentration.

[23] There are reports of sample water contamination by tritium leaking from a foreign-made radioluminous watch; hence, caution is necessary during distillation operations and sample collection.

- Rotary evaporator
- Water bath
- Aspirator (or diaphragm-type vacuum pump may be used)
- Conductivity meter

(2) Reagents
- Sodium peroxide (Na_2O_2): granular (purity ≥95%)
- Potassium permanganate ($KMnO_4$): JIS special grade reagent
- Silver nitrate ($AgNO_3$) solution: Dissolve 1 g silver nitrate in 100 mL 0.1 mol/L nitric acid.
- Conductivity standard solution (~140 mS/m)

(3) Procedure

1) Take the sample water[24] in an eggplant-shaped flask[25], add sodium peroxide and potassium permanganate at approximately 0.1 w/w% of the sample volume[26], and dissolve them in the water[27]. Note that glassware shall be thoroughly dried before use.
2) Assemble the distillation apparatus, ensure the flow of cooling water, switch ON the rotary evaporator, and rotate the eggplant-shaped flask at approximately 60 revolutions per minute.
3) Switch ON the aspirator and open the vacuum cock to confirm that reduced pressure is maintained inside the cylindrical distillation tube.
4) Switch ON the water bath, and set the water temperature to approximately 55°C.
5) The distilled water is collected in the round-bottom flask, and distillation is continued until the sample is dry. Take care to prevent the vigorous boiling of the sample[28].
6) After ensuring that the color of potassium permanganate is not the same as that at the area around the vacuum cock, turn the vacuum cock to return the pressure to normal.
7) Pour a few milliliters of the obtained distilled water into a beaker, add the silver nitrate solution into it in a drop-wise manner, and check whether or not a white precipitate (silver halide such as AgCl) is formed. If the water becomes cloudy, distill the obtained distilled water again. Alternatively, measure electrical conductivity using the electrical conductivity meter, and confirm that the electrical conductivity is approximately 1 mS/m or less (equivalent to the electrical conductivity of purified water produced by a commercially available water purifying apparatus)[29].

[24] The sample water amount is determined by considering the volume required for the measurement sample.

[25] Glassware such as flasks shall be thoroughly dried before use. Not only in this case, but in any tritium analysis, moisture can cause contamination; therefore, ensure that all equipment used are thoroughly dried.

[26] Sodium peroxide and potassium permanganate should be added at approximately 0.1 w/w% of the sample volume to decompose organic matter in the sample water. If there is no organic matter in the sample water, adding these reagents is not necessary.

[27] No boiling stones should be added.

[28] If bubbles begin to form vigorously, reduce the vacuum, increase the height of the eggplant-shaped flask to reduce the contact area with the water in the water bath, and increase the rotation speed of the eggplant-shaped flask to prevent vigorous boiling.

[29] If the distillate retains color due to potassium permanganate, repeat distillation.

8) The obtained distilled water should be used immediately to prepare the measurement sample or, if time is required, store it in a tightly sealed sample container (glass bottle, plastic container[30], etc.)[31].

[30] At sites where tritium sources are handled or where tritium is generated by nuclear reactions, tritium shall be stored in plastic containers with a sufficient degree of sealing equivalent to glass containers to prevent contamination by atmospheric vapor with high tritium concentration.

[31] There are reports of sample water contamination by tritium leaking from a foreign-made radioluminous watch; hence, caution is necessary during distillation operations and sample collection.

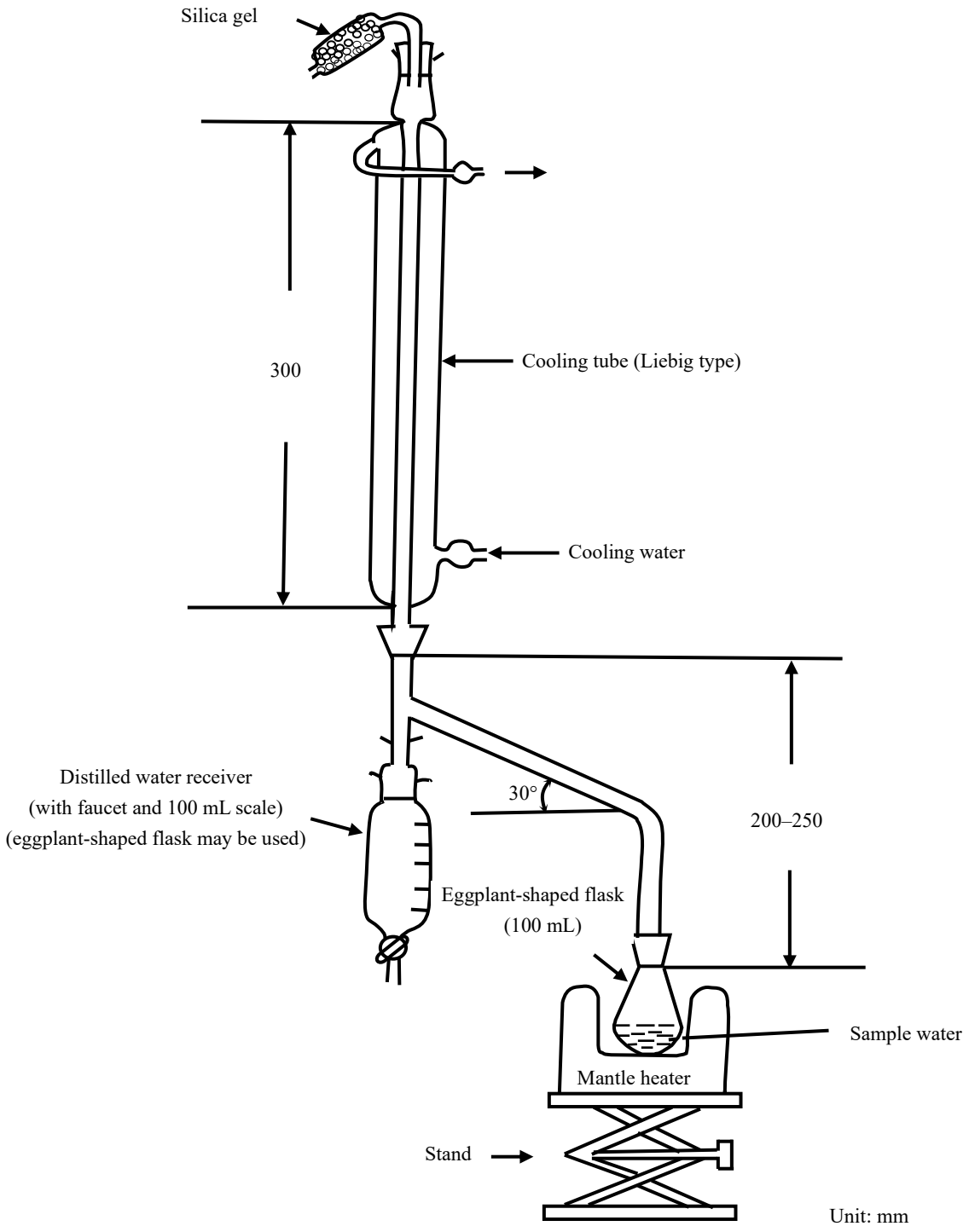


Figure 2.1 Schematic of an atmospheric distillation apparatus[32,33]

[32] Set a column packed with silica gel at the upper opening of the cooling tube to avoid pressurization and prevent water vapor from entering from outside.

[33] If the heater temperature is raised to a very high value, potassium permanganate may contaminate the distilled water, causing it to turn purple. Therefore, temperature should be properly controlled using branch pipes, etc.

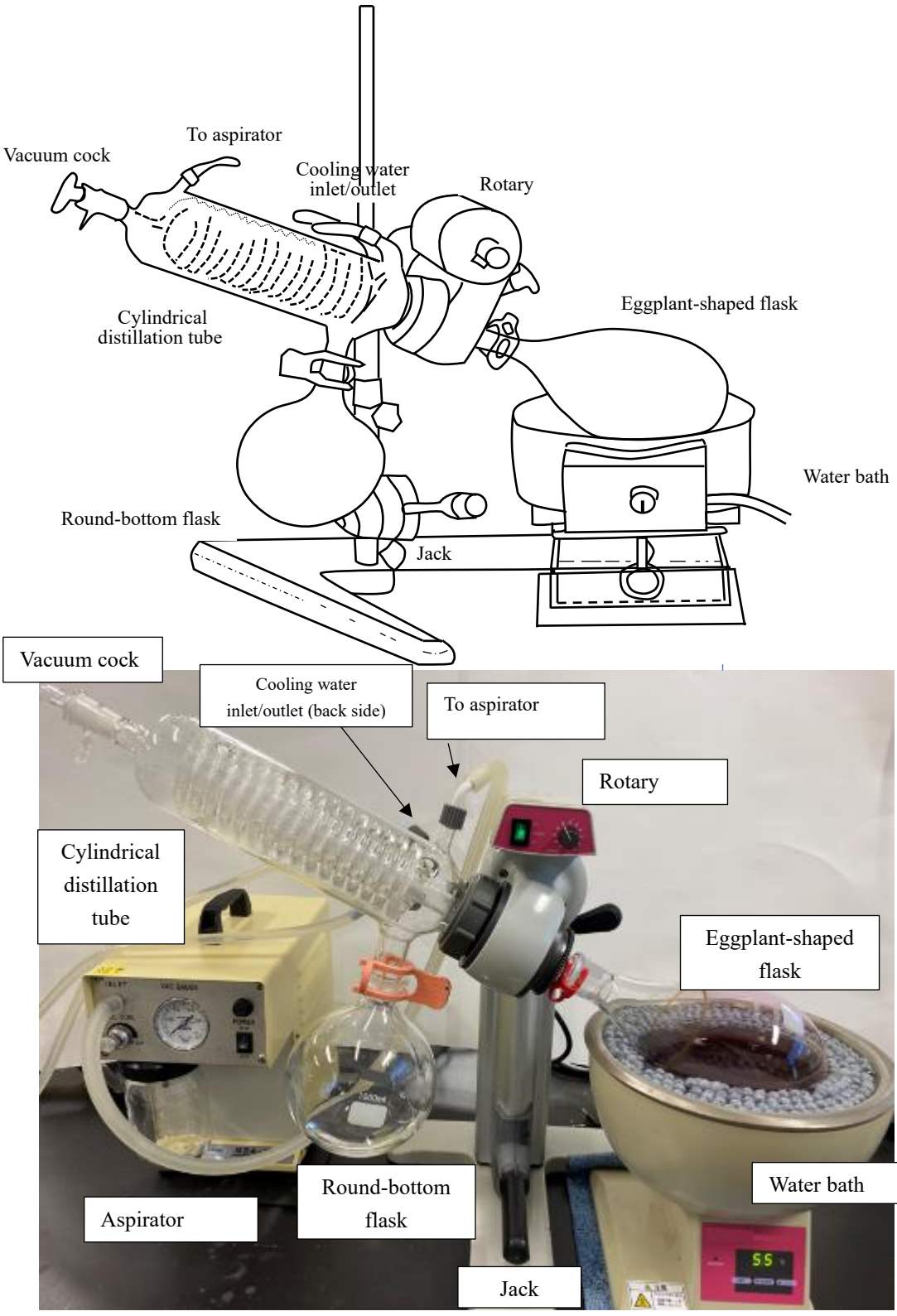


Figure 2.2 Example of Schematic of a vacuum distillation apparatus

2.3 Electrolytic enrichment of tritium

The current tritium concentration in the environmental water is very low, almost equal to or lower than the low DL of a liquid scintillation counter for low background (approximately 1 Bq/L). Furthermore, seawater has tritium concentration levels approximately one order of magnitude lower than that. To analyze such samples accurately, tritium must be enriched. Among methods used for enriching hydrogen isotopes, water electrolysis (electrolytic enrichment) is employed widely because it is relatively simple in terms of equipment and operation. The decision as to whether or not perform electrolytic enrichment should be made after carefully considering the purpose of the investigation and target DL.

There are two main methods for electrolytic enrichment: electrolyzing an aqueous alkaline solution using metal electrodes and a method that uses a solid polymer electrolyte (SPE). The characteristics of each method are described below.

[Electrolytic enrichment with metal electrodes]

- The tritium residual rate is approximately 0.7–0.8 when enriched from 500 mL to approximately 50 mL.

[Advantage]

- Multiple samples can be enriched simultaneously.

[Disadvantages]

- Hydrogen and oxygen gas are mixed together, which may cause an explosion.
- Electrolysis is time-consuming because current that can flow is small.
- Because electrolytes are added to the sample, the concentration ratio is limited. Furthermore, a post-electrolysis distillation is required.

[Electrolytic enrichment with a SPE]

- The tritium residual rate is approximately 0.6 when enriched from 1 L to approximately 70 mL.

[Advantages]

- Because no electrolytes are added to the sample, it can theoretically be enriched infinitely. Furthermore, distillation need not be performed after electrolysis.
- Owing to the generation of hydrogen and oxygen gas separately, the risk of explosion is low.
- Electrolysis is faster due to higher current flow.

[Disadvantages]

- Only one sample can be enriched at a time.
- If the SPE deteriorates, it must be replaced by the manufacturer.
- As a small amount of the sample remains on the electrode, care must be taken regarding cross-contamination between samples.

2.3.1 Electrolytic enrichment with metal electrodes

The analytical sample is purified via distillation in advance, and sodium peroxide is added to prepare an alkaline electrolyte solution. Metal electrodes made of iron[34] (cathode) and nickel (anode) are immersed in this electrolytic solution to perform electrolytic enrichment. The tritium enrichment ratio is calculated by electrolyzing a tritium aqueous solution of known concentration under the same conditions as samples and estimating the tritium residual rate (or recovery rate) before and after electrolysis and volume enrichment ratio (volume reduction ratio) of each sample.

(1) Apparatus
- Liquid scintillation counter (LSC)
- Incubator (thermostatic chamber)

(2) Laboratory equipment
- Complete set of vacuum distillation equipment (refer to 2.2.2 Vacuum distillation)
- Glass container
- Electronic balance (a minimum scale of 0.0001 and 0.01 g)
- Fixed quantity pipette
- Pipette tip
- Complete electrolysis cell (glass cell and metal electrodes are shown in Figure 2.3)
- Heating gun
- Vinyl tape
- Complete set of electrolytic enrichment equipment (water tank, cooling unit, holder for fixing, copper wire, silicon tube (for exhaust), DC power supply, and integrating ammeter) (Figure 2.4 shows a schematic of the electrolytic enrichment apparatus.)
- Eggplant-shaped flask (100 mL)
- Complete set of atmospheric distillation equipment (see 2.2.1 Atmospheric distillation)
- Measuring vials (fluoroplastic vials, etc.)

(3) Reagents
- Reagents required for vacuum distillation (refer to 2.2.2 Vacuum distillation)
- Reagents required for atmospheric distillation (refer to 2.2.1 Atmospheric distillation)
- Tritium standard solution (with a concentration of approximately 10 Bq/L at the time of use)
- Hydrochloric acid (10 mol/L, prepared immediately before use)
- Sodium hydroxide
- Pure water
- Boiling stones
- Emulsified scintillator
- Tritium-free water
- Lead chloride

(4) Procedure

[Preparation of samples with known tritium concentrations][35]

[34] A nickel metal electrode may be used as the cathode. Refer to Explanation A for details.

[35] This description is based on a sample water volume of 500.00 g and a measurement sample volume of 50.00 g. The amounts of test sample, measurement sample, and reagents and integrated current value can be changed appropriately depending on reaction conditions.

1) Add 2.53 g sodium peroxide to a cleaned and dried glass container and dissolve it with a small amount of pure water.
2) Add 10 g of tritium standard solution weighed accurately to four decimal places to the glass container. At this time, weigh accurately to four decimal places.
3) Add pure water to the glass container until the weight, excluding that of the glass container, is 505.00 g.
4) Repeat the above procedure to prepare two samples with known tritium concentrations.

[Preparation of analysis samples]

5) Distill approximately 600 g analysis sample under reduced pressure (refer to 2.2.2 Vacuum distillation).
6) Add 2.53 g sodium peroxide to a cleaned and dried glass container and dissolve it in some distilled sample water.
7) Prepare the sample water for electrolysis by adding the sample water to the glass container until the weight, excluding that of the glass container, is 505.00 g.
8) If there is more than one sample to be analyzed, repeat the above procedure.

[Etching of the electrode]

9) Remove the metal electrode from the storage solution (alkaline solution), wash it thoroughly with tap water, and then immerse it in 10 mol/L hydrochloric acid for 1 min to dissolve the surface.
10) Quickly wash the metal electrode with tap water (warm water) to wash off any remaining hydrochloric acid.
11) Wash the metal electrode with pure water.
12) Wipe off any moisture on the silicone plug and gas exhaust hole.
13) Dry the metal electrode with a heating gun or via other means.
14) Repeat the above operation for all metal electrodes to be used.

[Preparation of the electrolyte]

15) Measure the weight (W1) of the cleaned and dried glass cell.
16) Add 500.00 g sample water for electrolysis to the glass cell and record the weight at that instant as W2.
17) Insert a cleaned and dried metal electrode into the glass cell and record the weight at that instant as W3.
18) Insert the silicone stopper tightly in the mouth of the glass cell and wrap it with plastic tape to prevent gas leakage (Figure 2.5).
19) If there is more than one sample to be analyzed, repeat the above procedure for each sample.

20) Perform the above operations for samples with known tritium concentrations similarly.

[Electrolytic enrichment operation]

21) Immerse each electrolysis cell in a water tank cooled[36] to approximately 4°C–5°C[37], and secure in correct position to prevent any movement due to buoyancy. Connect each electrode terminal in series with a copper wire.

22) Attach a silicone tube to the gas exhaust hole to direct the generated gas (oxygen–hydrogen detonating gas) outdoor.

23) Connect the DC power supply to the electrode terminals.

24) Press the reset button on the integrating ammeter to set the display of integrated current (Ah) to zero.

25) Switch ON the DC power supply, apply a current of approximately 1 A, and confirm the commencement of electrolysis.

26) Set the current at 5 A and continue electrolysis for approximately 240 h (approximately 10 days) until the electrolyte amount reaches approximately 100 g[38] (Figure 2.6).

27) When the electrolyte amount reaches approximately 100 g, gradually reduce current (approximately 2 A), and continue electrolysis until the electrolyte reaches approximately 55 g. In this case, estimate the amount of electricity flowing through the cell using the integrating ammeter, and finally, stop electrolysis when integrated current reaches a value of 1300 Ah.[39]

28) Set the current to 0 A and switch OFF the DC power supply.

29) Remove the silicon tube and copper wire, remove the electrolysis cell from the water tank, and thoroughly wipe off any moisture on the outer wall of the electrolysis cell.

[Preparation of measurement sample and liquid scintillation measurement][40]

30) Remove the vinyl tape to replace the hydrogen gas inside the electrolysis cell with air and measure the weight (W4).

31) Transfer the electrolytically enriched sample water to an eggplant-shaped flask, add approximately 1 g lead chloride[41] to neutralize alkali (a reddish-brown precipitate of lead hydroxide is produced), and add a small number of boiling stones. Thoroughly rinse metal electrodes with tap water and store them in a 0.5 w/v% sodium hydroxide solution to prevent oxidation by air.

32) Assemble the atmospheric distillation apparatus, connect the eggplant-shaped flask containing sample water, and distill until dry. The dry solid matter remaining after distillation is lead oxide. Estimate electrical conductivity after distillation (strong alkalinity will interfere with liquid scintillation measurements) (refer to 2.2.1 Atmospheric distillation).

33) Weigh the distillate into a measuring container, add the emulsified scintillator, and shake thoroughly to prepare a uniform mixture.

34) Further, prepare two background samples using tritium-free water.

35) Keep the measurement sample in an incubator at approximately 15°C for a period of one day to one week.

---

[36] The cooling unit (cooling water circulator) must have sufficient cooling capacity considering the water tank size and total heat generated due to electrolysis. It is also necessary to pay attention to variations in water temperature inside the tanks, circulate the cooling water sufficiently, and control the temperature inside each electrolysis cell to maintain it at approximately 4°C to 5°C.

[37] As the temperature decreases, evaporation losses decrease. If antifreeze is used for cooling water, the temperature can be lowered even further; nevertheless, care shall be taken to ensure that the sample water does not freeze.

[38] Estimated from integrated current.

[39] Electrolysis takes approximately 14 days.

[40] For more information on liquid scintillation measurements, refer to the Measurement section.

[41] If the eggplant-shaped flask is not reused, adding lead chloride is not necessary.

36) Set the measurement sample in the designated place on the LSC.

37) Perform the measurement for approximately 500–1000 min.

38) Prepare and measure samples with known tritium concentrations in the same manner. However, because a sufficient counting rate can be obtained, it is enough to measure for approximately 200 min.

[Calculation of the tritium concentration][42]

39) Subtract the background counting rate from the counting rate of the sample with a known tritium concentration to obtain the net counting rate.

40) Calculate the tritium concentration Tf (Bq/mL) of the sample with a known tritium concentration after electrolytic enrichment from the net counting rate, counting efficiency, measured sample volume, and decay correction factor. The decay correction date[43] is the electrolysis completion date.

41) Calculate the tritium concentration Ti (Bq/mL) of the sample with a known tritium concentration before electrolysis, and then calculate the tritium enrichment ratio $F_{std} = Tf/Ti$ and tritium residual ratio $R = (Tf \times Vf)/(Ti \times Vi)$. The decay correction date is the electrolysis completion date.

42) Similarly, determine the net counting rate for analysis samples.

43) For each analysis sample, the tritium concentration after enrichment is calculated from the net counting rate, counting efficiency, measured sample volume, and decay correction factor. The decay correction date[44] is the sampling date.

44) Calculate the tritium enrichment ratio F_{sample} for each analysis sample from the volume enrichment ratio $N = Vi/Vf$ and tritium residual ratio R, and record it in the record book for tritium electrolysis enrichment (Figure 2.7) together with various measurement results from 1) to 43).

45) Divide the tritium concentration for each analysis sample by the tritium enrichment ratio F_{sample}[45] to calculate the tritium concentration in the water sample before enrichment.

46) If there is more than one sample to be measured, repeat the calculation for each analysis sample.

---

[42] Specific calculation examples are provided in Explanation F.

[43] To calculate the tritium enrichment ratio F_{std} from the ratio of the tritium concentration (Bq/L) in samples with a known tritium concentration before and after electrolysis and tritium residual ratio R from the radioactivity ratio (Bq), it is necessary to unify the decay correction date between the calculation of the tritium concentration before electrolysis and measurement of the tritium concentration after electrolytic enrichment. If the decay correction date is the same for both cases, it does not have to be the electrolysis completion date.

[44] Note that the decay correction date of the analysis sample is not the same as the electrolysis completion date.

[45] Be careful not to use the tritium enrichment ratio F_{std} for samples with known tritium concentrations.

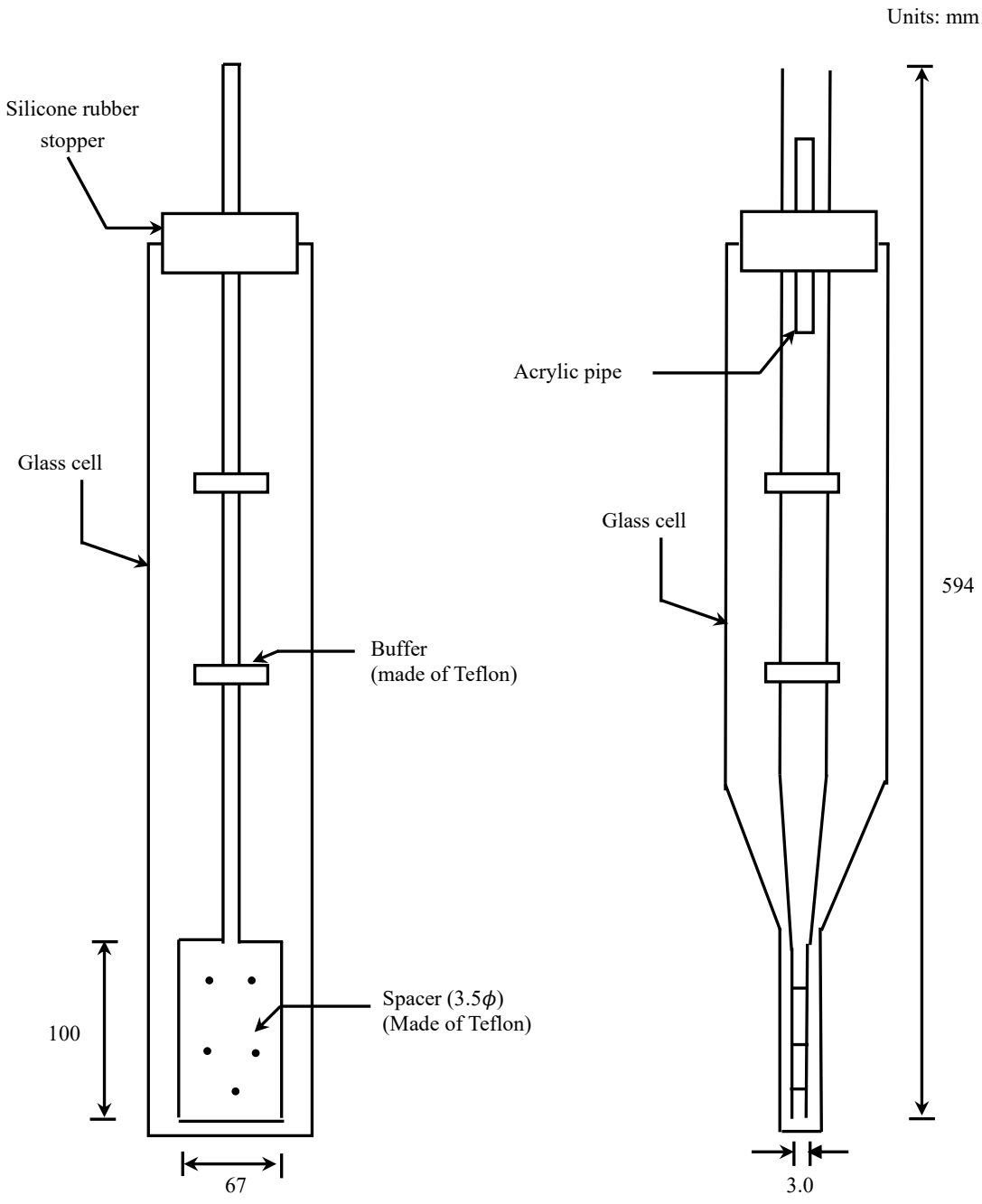


Figure 2.3 Examples of shapes of metal electrodes and glass cells

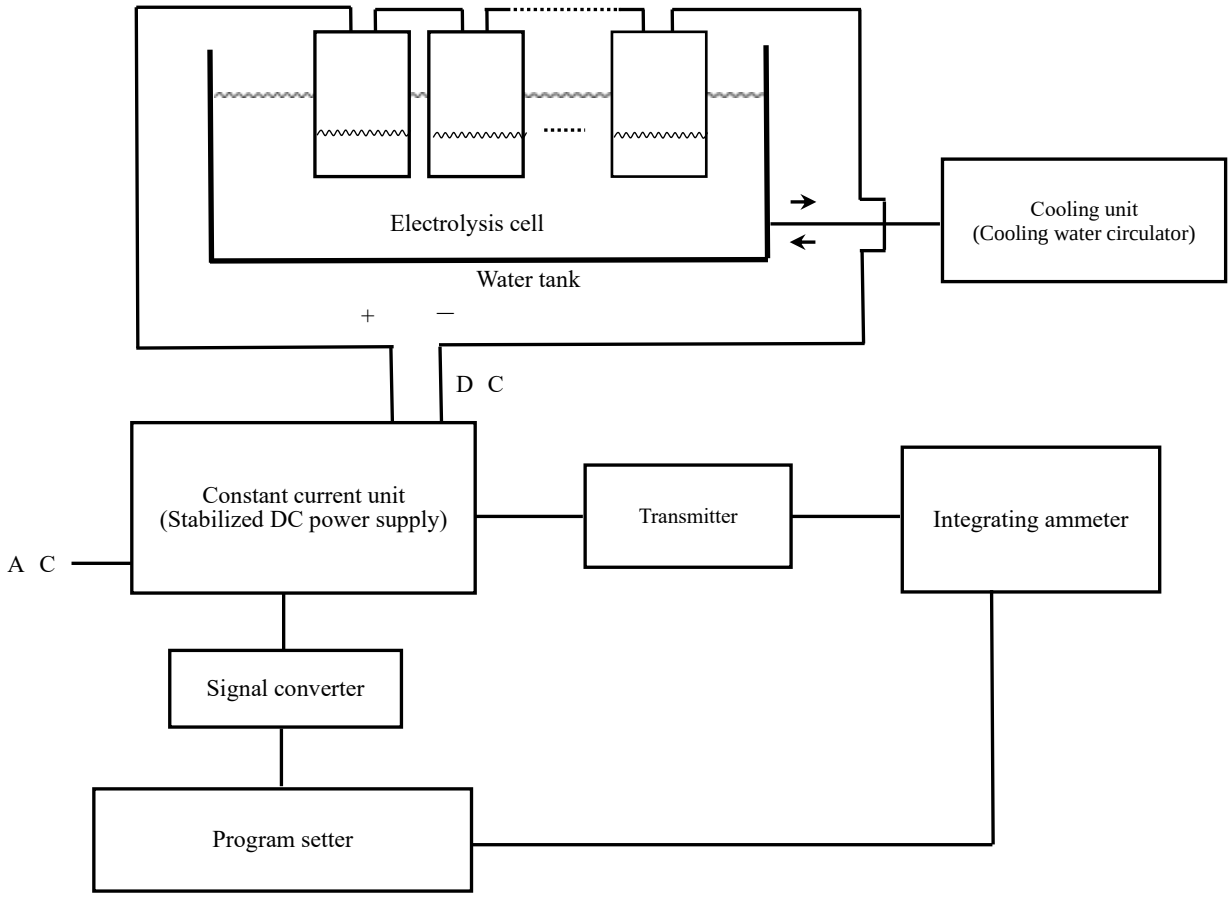


Figure 2.4 Schematic of an electrolytic enrichment apparatus (Example)

Figure 2.5 Electrolysis cell for electrolytic enrichment with metal electrodes (before electrolysis)

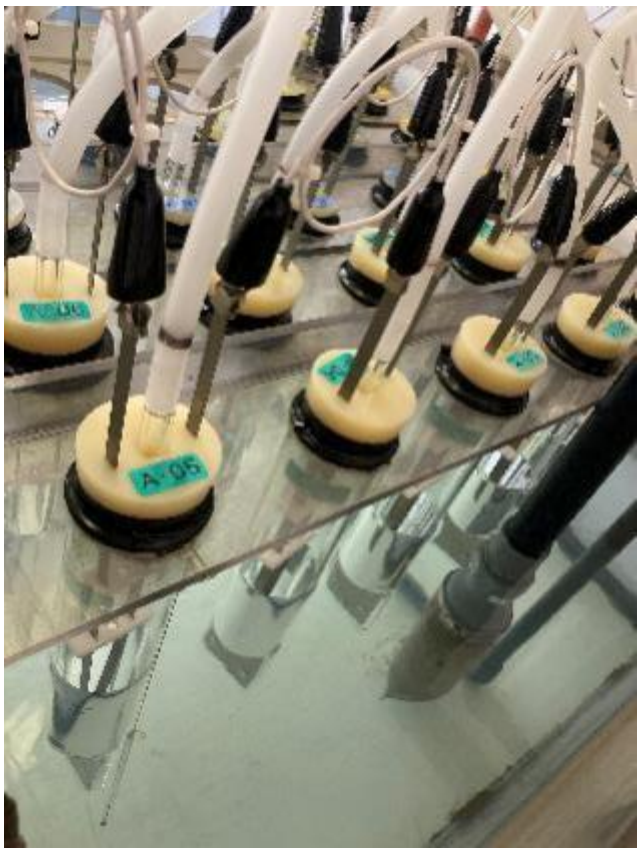


Figure 2.6 Electrolytic enrichment with metal electrodes

Tritium electrolytic enrichment record book

Electrolysis sample preparation date:
Electrolysis start date:
Electrolysis end date:
Measurement sample preparation date:

Electrode name: :
Power source No: :
Integrated current (AH): (÷ 2.98 :)

Sample cell No	Organization	Analysis No	Na_2O_2 (2.53g)	Na_2O_2+ sample (505g)	Cell (W1)	Cell + electrolyte (W2=W1+500)	W2 + electrode (W3)	After electrolysis (W4)	Vi Volume before enrichment	Vf Volume after enrichment	Experimental value – theoretical value	N Volume enrichment ratio (VI / VT)	F Enrichment ratio of each sample (N·R)	Vial (g)	Vial + sample (g)	Measurement sample weight (g)
2																
3																
4																
5																
6																
7																
8																
9																
1																
10																

The values below are calculated from added weight and specific radioactivity at the end of electrolysis ↓

std No.	Vial (g)	Std + vial (g)	STD(g)	TiVi(Bq) Radioactivity before enrichment	Concentration at the end date of electrolysis: Ti (Bq/L) Before electrolysis — Radioactivity concentration before enrichment	Concentration at the end date of electrolysis: Tf (Bq/L) After electrolytic enrichment — Radioactivity concentration after enrichment (measured value)	Tf/Ti Tritium enrichment ratio	R Tritium residual ratio
STD-1								
STD-2								
					Mean value of two standards			

Specific radioactivity of standard when preparing standard solution

Bq/g at

Specific radioactivity of standard at the end date of electrolytic enrichment

Bq/g at

H.L.(Y)
DAY=
DF=

←Calculate the enrichment ratio F for each sample using this R

Vi = (W2 - W1) * 0.995

Vf = Vi - (W3 - W4)

Experimental value – theoretical value = (Vi-Vf) – theoretical value

Ti = Radioactivity concentration of standard at the end date of electrolysis

N = Vi / Vf : Volume enrichment ratio

R = Tf Vf / Ti Vi : Mean value of two standards (tritium residual ratio)

F = N * R : Enrichment ratio of corresponding sample

Tf = Radioactivity concentration of standard after enrichment at the end date of electrolysis

Figure 2.7 Example of record book for tritium electrolytic enrichment

2.3.2 Electrolytic enrichment with solid polymer electrolyte (SPE)

Solid polymer electrolyte (SPE) is a type of cation exchange resin in which a polymer chain is chemically bonded with the sulfonic acid group to perform ionic conduction. The electrolytic part comprises an SPE membrane with both sides sandwiched between porous metal electrodes. When electric current flows between the electrodes, the generated hydrogen ions move through the SPE, producing oxygen gas at the anode and hydrogen gas at the cathode. SPE enrichment devices are commercially available for purchase.

The analysis sample is distilled and purified in advance to prepare an electrolytic solution. The electrolytic solution is electrolytically enriched using the SPE enrichment device. Calculate the tritium radioactivity concentration using the device constant Z determined in advance.

(1) Apparatus
- Liquid scintillation counter (LSC)
- Incubator (thermostatic chamber)
- Complete solid polymer electrolytic enrichment device (Figures 2.8 and 2.9)

(2) Laboratory equipment
- Complete set of vacuum distillation equipment (refer to 2.2.2 Vacuum distillation)
- Glass container
- Absorbent cotton, etc.
- Eggplant-shaped flask (100 mL)
- Electronic balance (min. scale 0.01 g)
- Fixed quantity pipette
- Complete set of atmospheric distillation equipment (see 2.2.1 Atmospheric distillation)
- Measurement container (fluoroplastic vial, etc.)

(3) Reagents
- Reagents required for vacuum distillation (refer to 2.2.2 Vacuum distillation)
- Tritium-free water
- Reagents required for atmospheric distillation (refer to 2.2.1 Atmospheric distillation)
- Emulsified scintillator

(4) Procedure

[Preparation of analysis sample][46]

1) Distill approximately 1100 g analysis sample under reduced pressure (refer to 2.2.2 Vacuum distillation).
2) Store distilled sample water in a glass container.

[Equipment washing]

3) Wipe the cell surface of the SPE enrichment device with absorbent cotton, etc.
4) Add tritium-free water[47] to the cell and perform electrolysis for washing at a current of approximately 10 A for approximately 10 min.
5) Open the valve at the sample water outlet and drain tritium-free water.
6) Add tritium-free water again, and repeat washing electrolysis.

[46] The procedure is for a sample water volume of 1000 g. The amount of sample, reagents, and integrated current value should be changed according to actual electrolysis conditions.

[47] Pure water or sample water may be used instead of tritium-free water. However, the water sample must be used for the third washing.

7) Add sample water to the cell and perform washing electrolysis similarly.

8) Open the valve at the sample water outlet and drain water until only a small amount of liquid remains inside electrodes.

9) Wipe the cell wall with absorbent cotton or similar material.

10) Drain thoroughly so that no liquid remains inside electrodes.

11) Immediately add 1000 g distilled sample water into the sample water tank[48].

[Electrolytic enrichment operation]

12) Switch ON the breaker of the electrolytic enrichment device.

13) Wait until the temperature of the electronic cooler at the exhaust gas outlet drops to the set temperature of 1°C–2°C.

14) Switch ON the rectifier and press the output key.

15) Press the electrolysis button.

16) Turn the current and voltage knobs on the front of the rectifier to set current at approximately 10 A and start electrolysis.

17) Switch ON the cooling fan[49] to cool the electrodes.

18) Gradually increase the current until it reaches 50 A.

19) Under conditions of 1000 g water sample and an electrolysis current of 50 A, the device stops automatically after approximately three days[50].

20) After electrolysis stops automatically, wait for water droplets on cell walls to fall off and for the electrolysis end lamp to go out.

21) Press the electrolysis button, and re-electrolyze at approximately 10 A.

22) After electrolysis stops automatically, set the current and voltage knobs to zero and turn OFF the output key and power supply of the rectifier.

23) Turn OFF the breaker of the electrolytic enrichment device.

24) Open the valve on the sample water outlet and pour the enriched water[51] into a 100 mL eggplant-shaped flask.

25) Clean the equipment for the next electrolytic enrichment process.

26) When high-concentration tritium water is electrolyzed, ensure that any residual tritium derived from the sample due to the memory effect has disappeared[52].

[Preparation of measurement sample and liquid scintillation measurement][53]

27) Transfer the electrolytically enriched sample water to an eggplant-shaped flask and add a small number of boiling stones.

28) Assemble the atmospheric distillation apparatus, connect the eggplant-shaped flask containing sample water, and distill until dry (refer to 2.2.1 Atmospheric distillation).

29) Weigh the distillate into a measurement container, add the emulsified scintillator, and shake thoroughly to prepare a uniform mixture.

30) Further, prepare two background samples using tritium-free water.

---

[48] Avoid leaving the electrodes empty for long duration so as to prevent the SPE from drying out.

[49] Some models come with an attached cooling fan, and some fans operate automatically when the electrolysis button is pressed.

[50] If the electrolyte remains at the sensor level for more than 3 min, current will automatically stop flowing.

[51] The sensor position for the enriched water is determined in advance according to the measurement sample.

[52] Refer to Explanation A for details.

[53] For more information on liquid scintillation measurements, refer to 6.1 Preparation of measurement samples and 6.2 Measurement.

31) Keep the measurement sample in an incubator at approximately 15°C for a period of one day to one week.
32) Set the measurement sample in the designated place on the LSC.
33) Perform the measurement for approximately 500–1000 min.

[Calculation of tritium concentration]

34) After subtracting the background counting rate from the counting rate of the measurement sample to obtain the net counting rate, calculate the tritium concentration of the enriched water from the counting efficiency and measurement sample volume.
35) Divide the obtained tritium concentration of the enriched water by the instrument constant $Z = Tf/Ti$ to calculate the tritium concentration of the analyzed sample[54].

[54] The instrument constant Z is the ratio of the tritium concentration before and after enrichment Tf/Ti. The sample water with a known concentration (approximately 10 Bq/L) is electrolytically enriched several times, tritium concentration after enrichment is measured, tritium enrichment ratios before and after electrolysis are obtained, and average value is used.

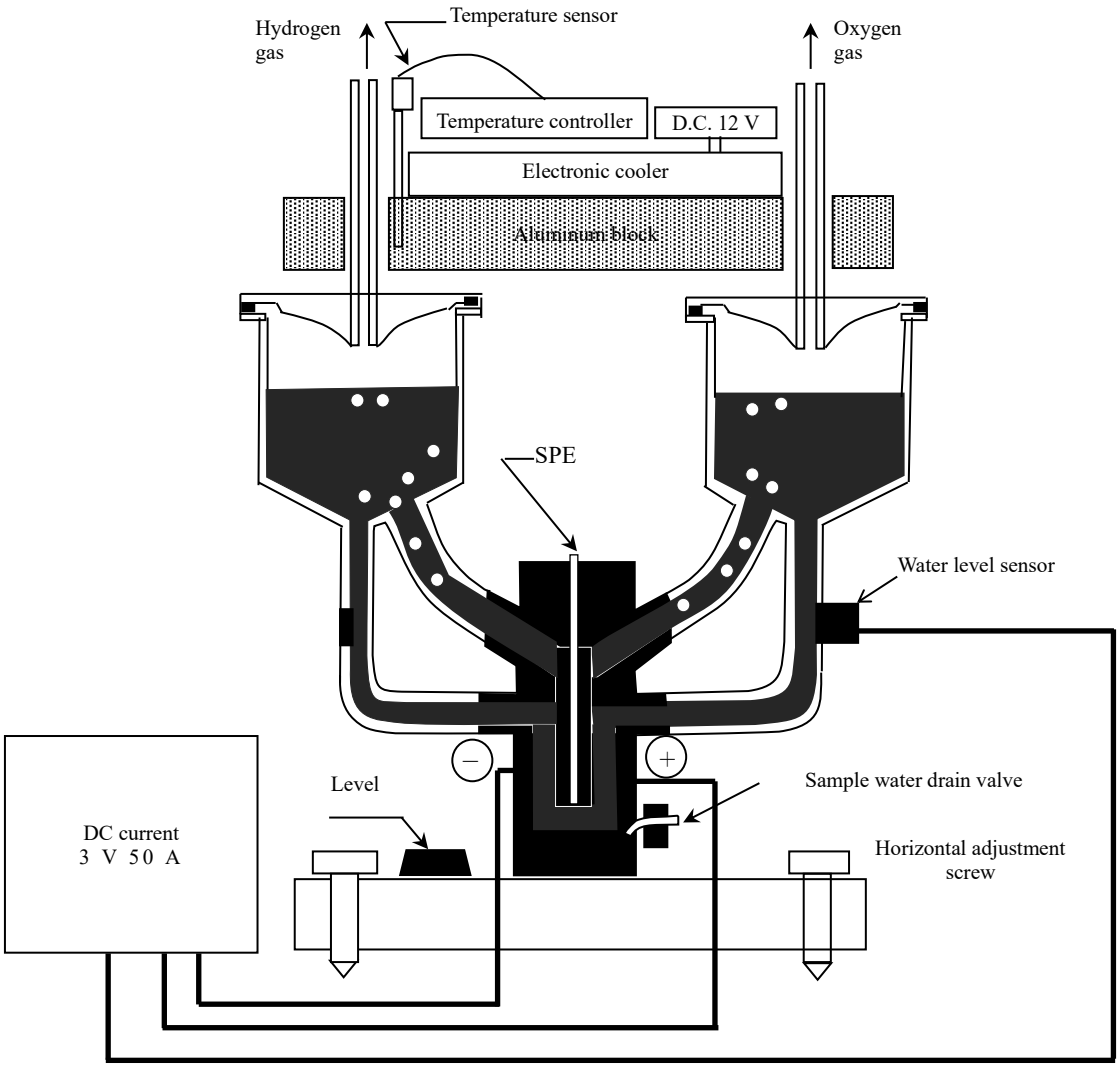


Figure 2.8 Schematic of the solid polymer electrolytic enrichment device

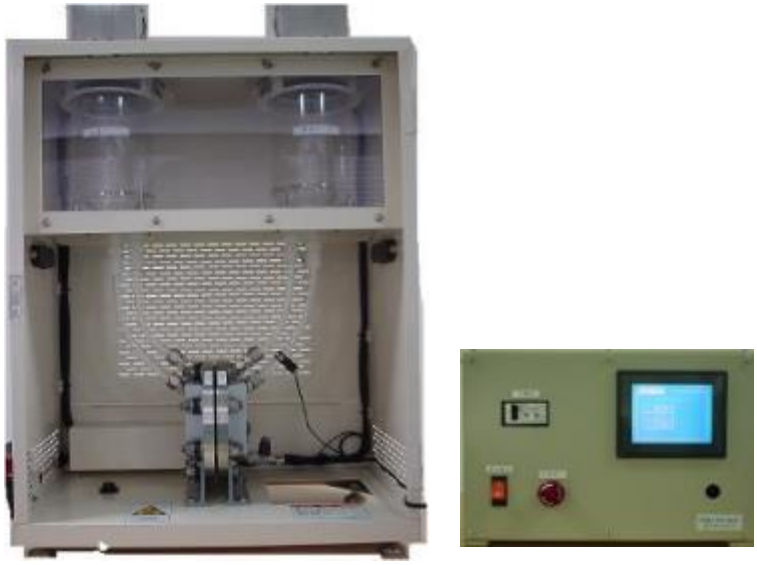


Figure 2.9 Schematic of the solid polymer electrolytic enrichment device

Chapter 3 Atmospheric Samples

Tritium in the atmosphere can be broadly divided into water vapor (tritiated water; hereinafter referred to as HTO), hydrogen gas (hydrogen–tritium; hereinafter referred to as HT), and organic tritium (such as CH_3T). Because CH_3T is present in extremely small amounts and very few organizations currently use it for monitoring, this analysis method targets HTO and HT in atmospheric samples. Note that HTO is more important for evaluating the radiation exposure dose, and it is not necessarily required to monitor together with HT. Because these types of tritium have different chemical properties, methods that are appropriate for their properties are used when collecting tritium.

HTO collection methods include (1) hygroscopic method using molecular sieve (the hygroscopic capacity and adsorbed HTO amount are stable with respect to changes in the relative humidity), (2) hygroscopic method using silica gel (collection accuracy is slightly poor, but the hygroscopic capacity can be easily visualized owing to the color change), (3) method using dehumidifier (collection accuracy is quite poor, but the method is straightforward), (4) passive method (low cost and does not require electricity; therefore, effective for collection at multiple locations), (5) bubbling method (sample is diluted in a trapping solution; therefore, requires electrolytic enrichment to reach the same detectable level as other methods), and (6) cooling and flocculation method (collection principle is similar to the method using dehumidifier, but the flow rate is adjustable). To calculate the atmospheric tritium concentration using the (3) method with a dehumidifier, (4) passive method, (5) bubbling method, and (6) cooling and flocculation method, the water amount per unit volume in the atmosphere must be determined separately.

HT collection methods include the (1) hygroscopic method using molecular sieves (where dry air, which has been passed through molecular sieves in the preceding stage to remove HTO, is passed through a palladium oxidation catalyst after tritium-free hydrogen gas to be converted to water is added as a carrier, and the resulting water is collected in molecular sieves) and (2) bubbling method (where air, which has been passed through a trapping solution in the preceding stage to remove HTO, is converted to water through a platinum–alumina catalyst column heated in an electric furnace, and the resulting water is collected in the trapping solution).

In the method using a desiccant, the HTO and HT collected in the form of water are recovered by heating the column in an electric furnace to bake out the collected water, and the water is recovered using the cold trap method. In the cooling and flocculation method, water that has been

heated and dissolved is recovered. The electrical conductivity of the collected water is measured, and if necessary, water is distilled and purified to prepare the sample water for measurement. The bubbling method and cooling and flocculation method are described in Information B. The bubbling method described in Information B cannot discriminate between HT and organic tritium (e.g., CH_3T); another method is to pass air after collecting HTO and HT through a catalytic column heated in an oven to convert organic tritium (e.g., CH_3T) to water, and collect the resulting water in molecular sieves[55].

3.1 Sampling

3.1.1 Sampling location and frequency[56]

(1) Sampling location

In principle, sampling locations shall be set according to the purpose of the survey. When determining sampling locations from the perspective of environmental monitoring around nuclear facilities, it is desirable to consider the environmental conditions around the facility. In addition, setting comparison points that can serve as background data will be helpful when evaluating data.

(2) Sampling frequency

As a rule, samples should be collected continuously over a period of approximately 1–2 weeks.

3.1.2 Precautions for sample collection

(1) Sample volume

Although the water vapor amount in the atmosphere varies with the season (higher in summer and lower in winter), to ensure that 50 mL sample water is available for measurement, the collection flow rate or collection time (period) must be determined so that at least 70 mL can be collected, considering losses in the analysis process. The absolute humidity [g/m^3] obtained from the temperature and relative humidity is shown in

[55] N. Momoshima, T. Yamaguchi, T. Toyoshima, Y. Nagao, M. Takahashi, M. Takamura and Y. Nakamura, Tritium in the Atmospheric Environment, *Journal of Nuclear and Radiochemical Sciences*, **8(2)**, 117-120 (2007).

[56] This description is an example. When establishing the monitoring plan, refer to the NRA Guideline for Emergency Preparedness and Response and its Supplementary Reference Materials "Ordinary Monitoring" and " Emergency Monitoring."

Table 3.1 and may be used as a reference (refer to Explanation B for details on the calculation method).

For example, the absolute humidity at 25°C and 70% relative humidity is approximately 16 g/m^3, and approximately 4.4 m^3 of air is needed to collect more than 70 g water. Therefore, if the collection period is one week, the collection flow rate shall be set at 0.5 L/min or more. For the passive method[57], the collection period of approximately 2 weeks would be required to collect the same volume of water as that collected using 600 g hygroscopic material.

The aforementioned collection volume is based on the assumption that a 100 mL vial is used as the measurement container; a smaller volume may be used if a 20 mL vial is used.

Table 3.1 Absolute humidity (g/m^3)

		Relative humidity [%]									
		10	20	30	40	50	60	70	80	90	100
Temperature [°C]	0	0.48	0.97	1.45	1.94	2.42	2.91	3.39	3.88	4.36	4.84
	5	0.68	1.36	2.04	2.72	3.40	4.07	4.75	5.43	6.11	6.79
	10	0.94	1.88	2.82	3.76	4.70	5.63	6.57	7.51	8.45	9.39
	15	1.28	2.56	3.84	5.13	6.41	7.69	8.97	10.25	11.53	12.82
	20	1.73	3.46	5.18	6.91	8.64	10.37	12.09	13.82	15.55	17.28
	25	2.30	4.60	6.91	9.21	11.51	13.81	16.11	18.41	20.72	23.02
	30	3.03	6.07	9.10	12.13	15.16	18.20	21.23	24.26	27.30	30.33
	35	3.95	7.91	11.86	15.82	19.77	23.73	27.68	31.64	35.59	39.55

(2) Sample storage

The collected sample should be stored in a tightly sealed sample container (glass bottle, plastic container[58], etc.) to prevent evaporation and contamination by water vapor in the atmosphere. Furthermore, do not add acid.

(3) Sample records

Record and preserve the following as necessary:

[57] N. Akata, H. Kakiuchi, K. Kanno, N. Shima and S. Hisamatsu, Determination of the Atmospheric HTO Concentration around the Nuclear Fuel Reprocessing Plant in Rokkasho by Using a Passive Type Sampler, *Fusion Science and Technology*, **60(4)**, 1292-1295 (2011)

[58] At sites where tritium sources are handled or where tritium is generated by nuclear reactions, tritium shall be stored in plastic containers with a sufficient degree of sealing equivalent to glass containers to prevent contamination by atmospheric vapor with high tritium concentration.

Name of the sampling agency, name of the sampling person, sample name, sample number, date and time of sampling, sampling location, sampling conditions, sampling method, information on reagents (specifications, Lot No., etc.), information on gas (specifications, Lot No., etc.), volume collected, amount of water collected and sampling flow rate, weather, temperature, humidity, etc. on the collection day.

(4) Measures to prevent sample contamination

There are reports of sample water contamination by tritium leaking from a foreign-made radioluminous watch, so caution is necessary. In addition, the tritium concentration in environmental samples is extremely low, while samples from the working environment in nuclear facilities usually have much higher concentrations. Therefore, when samples with extremely different levels coexist, it is advisable to take measures such as storing them in sealed containers and separating storage areas to prevent the contamination of low-concentration samples.

(5) Location of the suction port and sampling device

As a rule, the suction ports used in methods that utilize molecular sieves or silica gel as well as dehumidifiers and passive samplers should be installed outdoors in a well-ventilated area that does not allow rainwater to enter, such as under the eaves of a building, and care should be taken to ensure that the location is not affected by artificial intake and exhaust, which should not be mixed with indoor air. When installed indoors, the equipment shall be installed at a location that allows sufficient outdoor air to be drawn in, considering the same issues as those faced during outdoor installation.

3.2 Sampling methods

3.2.1 Methods using molecular sieves

These methods use molecular sieves as moisture absorbing material to separate and collect HTO and HT in air according to their chemical forms. The following equipment, laboratory instruments, reagents, and gases are required for this method.

(1) Apparatus

・ Atmospheric tritium collector (Figure 3.1)

- Tube furnace (Figure 3.2)

(2) Laboratory equipment

- Glass column (for molecular sieves) (Figure 3.3)
- Glass column (for palladium catalyst) (Figure 3.3)
- Electrolysis cell (nickel electrode) (Figure 3.4)
- Column case (Figure 3.5)
- Cold trap (Figure 3.6)

(3) Reagents and gases

- Palladium catalyst (0.5% Pd– alumina)
- Molecular sieves (3A, etc.)
- Sodium peroxide (Na_2O_2): granular (≥95% purity)
- Tritium-free water (water with an extremely low tritium concentration such as deep-sea water, deep groundwater, etc.) Tritium-free water to be used must be precisely analyzed in advance using the electrolytic enrichment method, etc., to confirm that the tritium concentration is below the DL of 60–70 mBq/L (refer to 5.2 Background sample preparation).
- Nitrogen gas (purity 99.999%)

(4) Procedure

1) Prepare four glass columns containing approximately 400 g[59] molecular sieve, four per sampling point (hereafter referred to as molecular-sieve columns). In humid seasons, the number of molecular-sieve columns may be increased by one. Similarly, prepare a glass column containing approximately 500 g palladium catalyst per sampling point (hereinafter referred to as palladium columns). If HT is not collected, two molecular-sieve columns should be prepared, and there is no need to prepare palladium columns and electrolytic cells.

2) To remove residual moisture, the molecular-sieve columns are baked in the tube furnace (400°C) for at least 4 h with nitrogen gas flowing at 200 mL/min, as shown in Figure 3.2. The palladium columns are baked in the electric furnace (180°C–200°C) with nitrogen gas flowing at 200 mL/min for at least 3 h. When used to collect samples with

[59] The vapor amount that can be adsorbed is approximately 20% of the molecular sieve mass.

high tritium concentrations, molecular sieves are washed with tritium-free water and then baked to minimize the influence of the memory effect.

3) Prepare a well-dried electrolysis cell with 150 g tritium-free water and 1–1.5 g sodium peroxide as the electrolyte.

4) The prepared columns and cells shall be named in the order of arrows shown in Figure 3.7 "Tritium Collector System Diagram", their weights shall be measured and recorded on Figure 3.8 "Tritium Collection Record Sheet" (weight at installation), and set in the column case.

5) Assemble the column case and connect it to the main body of the collector (Figure 3.1).

6) Record the value of the integrating flowmeter (integrated flow at installation).

7) Turn the pump switch ON and record the time (start time).

8) The appropriate sampling flow rate will vary depending on the season; however, the flow rate that produces the required sample volume should be set and recorded based on past data, and the absolute humidity is calculated from the temperature and relative humidity.

9) Current flowing through the electrolysis cell shall be set to approximately 1.3–1.5 A for a collection period of one week and a collection volume of approximately 70 mL (theoretically, the amount of water that will be decomposed is equivalent to the integrated current value [Ah] divided by 2.98 [g]; therefore, this value should be adjusted according to the collection period and amount of water collected). Record the current and voltage values.

10) Operate continuously for a certain period of 1–2 weeks.

11) Check daily for fluctuations in the set flow rate and current.

12) Turn the pump switch OFF. Record the time (collection time).

13) Record the value of the integrating flowmeter (integrated flow rate at collection).

14) Measure and record the weight of the column and cell (weight at collection).

15) Bake out the collected moisture from the molecular-sieve columns and palladium columns in the device shown in Figure 3.6 according to the conditions of Step 2. Moisture baked out of columns is collected in the cold trap.

16) Water collected from the HTO columns M1 and M2 (molecular-sieve columns) is combined to one sample. Water collected from the palladium column and HT column

(molecular-sieve column) is also combined to one sample. The former is used as the water sample for HTO measurement, while the latter is utilized as the water sample for HT measurement.

17) Subtract the weight and integrated flow values at the time of installation from the corresponding values at the time of collection for each column and calculate the weight increase (amount of water collected) and sampling flow rate Q for each column. The weight loss of tritium-free water is calculated by subtracting the weight at the time of collection from that at the time of installation of the electrolysis cell.

18) The following formula is used to determine the efficiency of HT oxidation using palladium (collection efficiency).

$$L = \frac{P + N}{C - D} \times 100$$

where

L: Oxidation efficiency (%)

P: Weight increase of the palladium columns (g)

N: Weight increase of the HT columns (molecular-sieve columns) (g)

C: Weight loss of tritium-free water in the electrolysis cell (g)

D: Weight increase of the dried columns (molecular-sieve columns) (g)

If the oxidation efficiency deteriorates, replace the column with a new one.

19) Record the oxidation efficiency (the oxidation efficiency value is used when calculating the HT concentration).

20) The sample collected at Step 16 should be used as the water sample for the measurement of HTO and HT.

3.2.2 Methods using silica gel

This method uses silica gel as a moisture absorbent to collect HTO from the atmosphere. The basic method and procedures for this method are the same as those when using molecular sieves; however, silica gel has inferior moisture absorption capacity than molecular sieves. Therefore, care must be taken when setting the amount and flow rate of silica gel.

In this section, the equipment, laboratory instruments, and reagents and gases required other than silica gel used as a moisture absorbent are the same as those described in 3.2.1 Methods using molecular sieve.

(1) Procedure

1) Fill the glass column with approximately 500 g[60] silica gel (1.98–2.36-mm granules, use the one that changes color when absorbing moisture), and prepare three columns per sampling location (hereinafter referred to as silica gel columns).

2) Silica gel columns are baked in the tube furnace (200°C) for at least 4 h with nitrogen gas flowing at 200 mL/min, as shown in Figure 3.2, to remove residual moisture. When used to collect samples with high tritium concentrations, silica gel should be washed with tritium-free water after use and then baked to minimize the influence of the memory effect.

3) The prepared columns are named in the order of arrows shown in Figure 3.7, "Tritium Collector System Diagram," and their weights are measured. After recording in the "Tritium Collection Record Form" (Figure 3.8) (weight at installation), set columns in the column cases.

4) Assemble the column case in the sampler body (Figure. 3.1) and connect.

5) Record the value of the integrating flowmeter (integrated flow at installation).

6) Turn the pump switch ON and record the time (start time).

7) Although the sampling flow rate varies greatly depending on the season, a flow rate that will produce the required sample volume should be set and recorded based on past records and the absolute humidity determined from the temperature and relative humidity.

8) Operate continuously for a certain period of 1–2 weeks.

9) Check daily for fluctuations in the set flow rate and silica gel for discoloration due to moisture absorption.

10) Turn the pump switch OFF. Record the time (collection time).

[60] The water vapor amount that can be adsorbed is approximately 20% silica gel weight at 50% relative humidity. However, care must be taken because the water vapor amount that can be adsorbed decreases as the relative humidity decrease. For adsorption performance, consult the manufacturer's technical data and the following literature. 村田敏, 榎本敏夫, 宮内樹代史: シリカゲル薄層の吸湿特性と固定層のシミュレーション,*農業機械学会誌*, **55(3)**, 41-49(1993).

11) Record the value of the integrating flowmeter (integrated flow rate at collection).

12) Measure and record the weight of the column and cell (weight at collection).

13) Bake out the collected moisture with the device shown in Figure 3.6 according to the conditions in the Step 2. Water baked out of the column is collected in the cold trap.

14) Water collected from the HTO columns (M1, M2, and M3 (silica gel columns)) is combined to serve as one sample.

15) Calculate the weight increase (collected amount) and sampling flow rate Q by subtracting the corresponding values at the time of installation from the values at the time of recovery for each column and value of the integrating flowmeter.

16) The sample collected at Step 14 is used as the water sample for HTO measurement.

3.2.3 Methods using a dehumidifier

In addition to the use of molecular sieve and silica gel as described in the 3.2.1 and 3.2.2 sections, there are other methods for collecting water vapor from the atmosphere such as using dehumidifiers or coolers or bubbling air through water. In these methods, only the specific radioactivity of HTO can be determined. To calculate the atmospheric tritium concentration, the water amount per unit volume in the atmosphere must be determined separately. This section describes a method for collecting water vapor from the atmosphere using a commercially available dehumidifier. The following equipment and laboratory instruments are required for this method.

(1) Apparatus

- Dehumidifier: Because the attached drainage tank may become full, connect a hose to the drainage port of the dehumidifier and continuously drain the dehumidified water into an external polyethylene container. (Figure 3.9)
- Thermo-hygrometer data logger

(2) Laboratory equipment

- Polyethylene container with a handle (approximately 40–50 L): Wash with pure water and dry in advance. It is recommended to drill a hole in the lid to pass a hose through.
- Sample container: Wash with pure water and dry.
- Hose: Prepare a hose of at least 50 cm length.

・ Stand: A platform on which the dehumidifier is placed. Choose a sturdy one.

(3) Procedure

1) Install dehumidifiers and the thermo-hygrometer data logger at the sampling location.

2) Connect the hose to a dry polyethylene container. The hose should always be sloped downward. Further, confirm that the hose is not bent in the middle.

3) Cover the polyethylene container with a lid to maintain it dust-free.

4) Switch ON the power and run the dehumidifier.

5) After a certain period of time (one week to one month), turn OFF the dehumidifier and transfer the water remaining in the hose to the polyethylene container.

6) Extract the temperature and humidity data from the thermo-hygrometer data logger.

7) Stir water in the polyethylene container and wash the sample container 2–3 times with dehumidified water.

8) Collect the required amount (0.5–2 L) of the dehumidified water in the sample container. Overflow the sample container with the dehumidified water and seal the container tightly. Note that, during the dry winter season, it may not be possible to collect the required amount. In this case, collect the entire dehumidified water in the polyethylene container.

9) Write the sample number, etc. on the sample container.

10) Discard the remaining water.

11) The sample collected in Step 8 should be used as the water sample for HTO measurement before purification.

3.2.4 Passive method[61]

Methods described in the 3.2.1–3.2.3 sections use electrical equipment such as pumps and dehumidifiers; nevertheless, there is a passive collection method that does not require a power source. In the passive method, a moisture absorbent is placed in a container separated by a porous membrane that allows gas to pass through, and water vapor in the air is collected via free diffusion. In this case, as in method 3.2.3, only the specific radioactivity of HTO can be determined. To

[61] N. Akata, H. Kakiuchi, K. Kanno, N. Shima and S. Hisamatsu, Determination of the Atmospheric HTO Concentration around the Nuclear Fuel Reprocessing Plant in Rokkasho by Using a Passive Type Sampler, *Fusion Science and Technology*, **60(4)**,1292-1295 (2011).

calculate the atmospheric tritium concentration, the water amount per unit volume in the atmosphere must be determined separately.

The following equipment, laboratory instruments, and reagents are required for this method.

(1) Apparatus

- Thermo-hygrometer data logger
- Tube furnace (Figure 3.2)

(2) Laboratory equipment

- Collection container[62]: Polyethylene (130-mm high and 110-mm ϕ with inner cap and outer screw cap). Drill a 70-mm ϕ hole in the inner cap and fix the porous permeable membrane with an acrylic modified silicone adhesive. The outer screw cap is used for storage before and after collection. (Figure 3.10)
- Porous permeable membrane: Ultrahigh-molecular-weight polyethylene porous film (1-mm thick)
- Stand: A platform on which the passive sampler is placed. Choose a sturdy one.
- Glass column (Figure 3.3)

(3) Reagents and gases

- Moisture absorbent: molecular sieve (3A, etc.) and silica gel
- Nitrogen gas (purity 99.999%)

(4) Procedure

1) Fill the collection vessel with approximately 300 g[63] hygroscopic material and measure the weight of the passive sampler at the time of installation.
2) Install the passive sampler and thermo-hygrometer data logger at the sampling location.
3) After a certain period of time (approximately 2 weeks to 1 month), measure the weight of the passive sampler at the time of collection and subtract the weight at the

[62] To increase the amount collected per unit time, install multiple collection vessels or use larger collection vessels to increase the surface area.

[63] The amount of water vapor that can be adsorbed is approximately 20% of the weight of the hygroscopic agent. However, care must be taken because the amount of water vapor that can be adsorbed by silica gel decreases as the relative humidity decrease. For adsorption performance of silica gel, consult the manufacturer's technical data and the following literature. 村田敏, 榎本敏夫, 宮内樹代史: シリカゲル薄層の吸湿特性と固定層のシミュレーション,*農業機械学会誌*, **55(3)**, 41-49(1993).

time of installation from that at the time of collection to calculate the weight increase (amount collected).

4) Extract the temperature and humidity data from the thermo-hygrometer data logger.

5) If molecular sieves are as a hygroscopic agent, collect water according to the Step 15 in the 3.2.1 section; if silica gel is used to collect water according to the Step 13 in the 3.2.2 section.

3.3 Purification of sample water

The electrical conductivity of the collected sample water is measured. If necessary, water is purified via distillation to obtain the sample water for tritium measurement. The purpose of distillation is the same as that in 2.2 Purification of Sample Water.

3.3.1 Atmospheric distillation

The laboratory equipment and reagents required for this method are the same as those listed in 2.2.1 Atmospheric distillation. The same is true for analytical operations.

3.3.2 Vacuum distillation

The laboratory equipment and reagents required for this method are the same as those listed in 2.2.2 Vacuum distillation. The same is true for analytical operations.

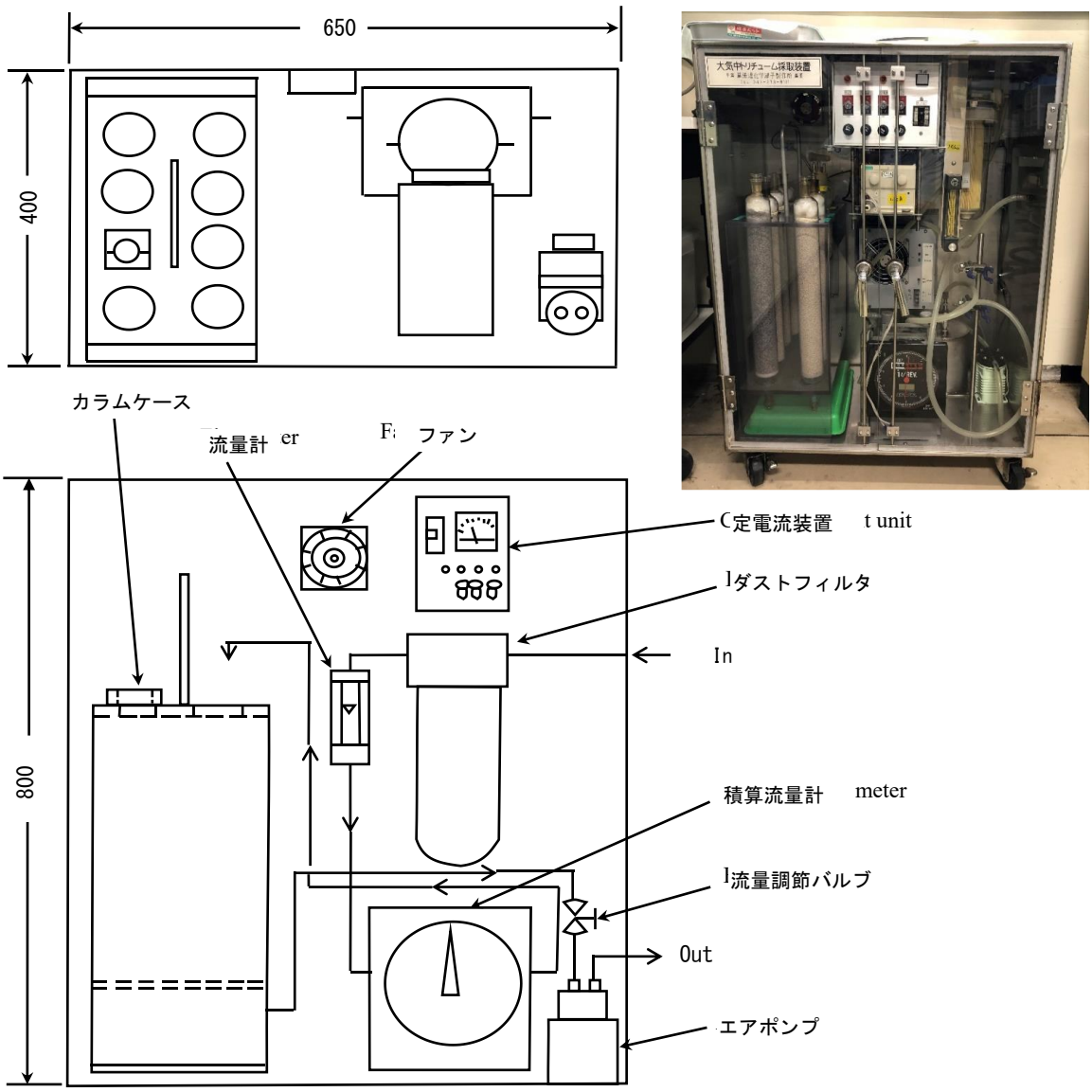


Figure 3.1 Schematic of an atmospheric tritium collector (Example)

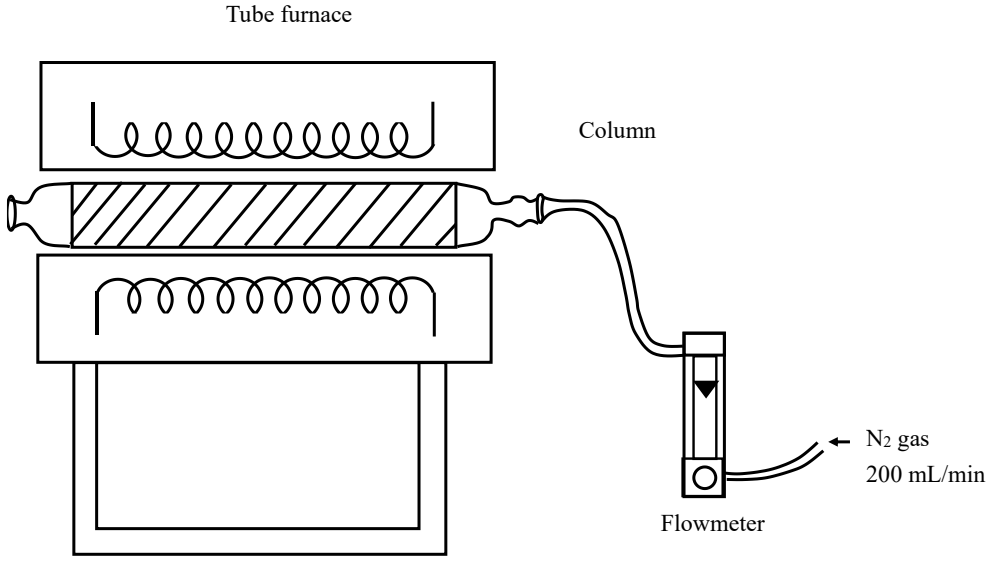


Figure 3.2 Schematic of a tube furnace (Example)

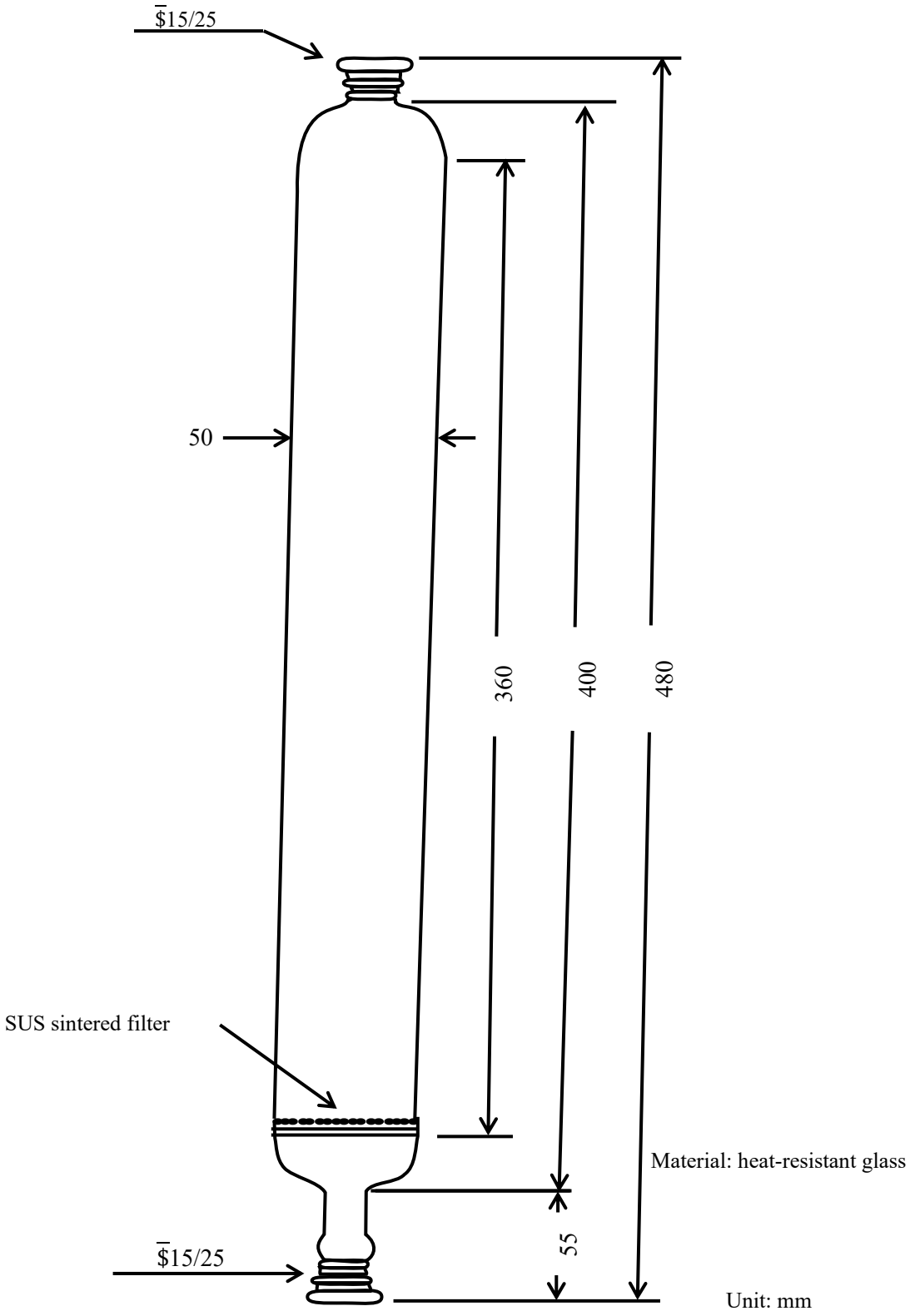


Figure 3.3 Schematic of a glass column (Example)

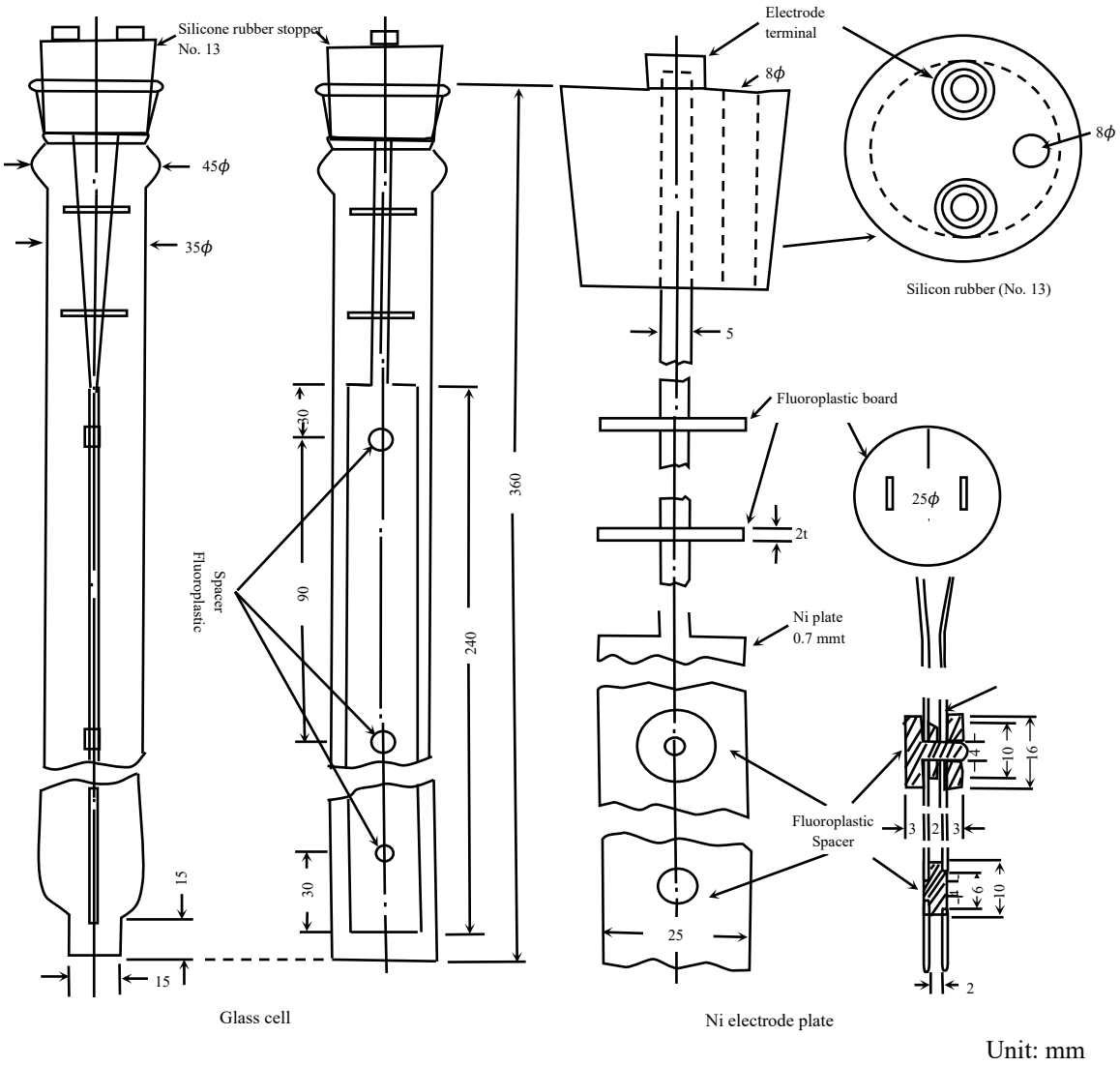


Figure 3.4 Schematic of an electrolysis cell (Example)

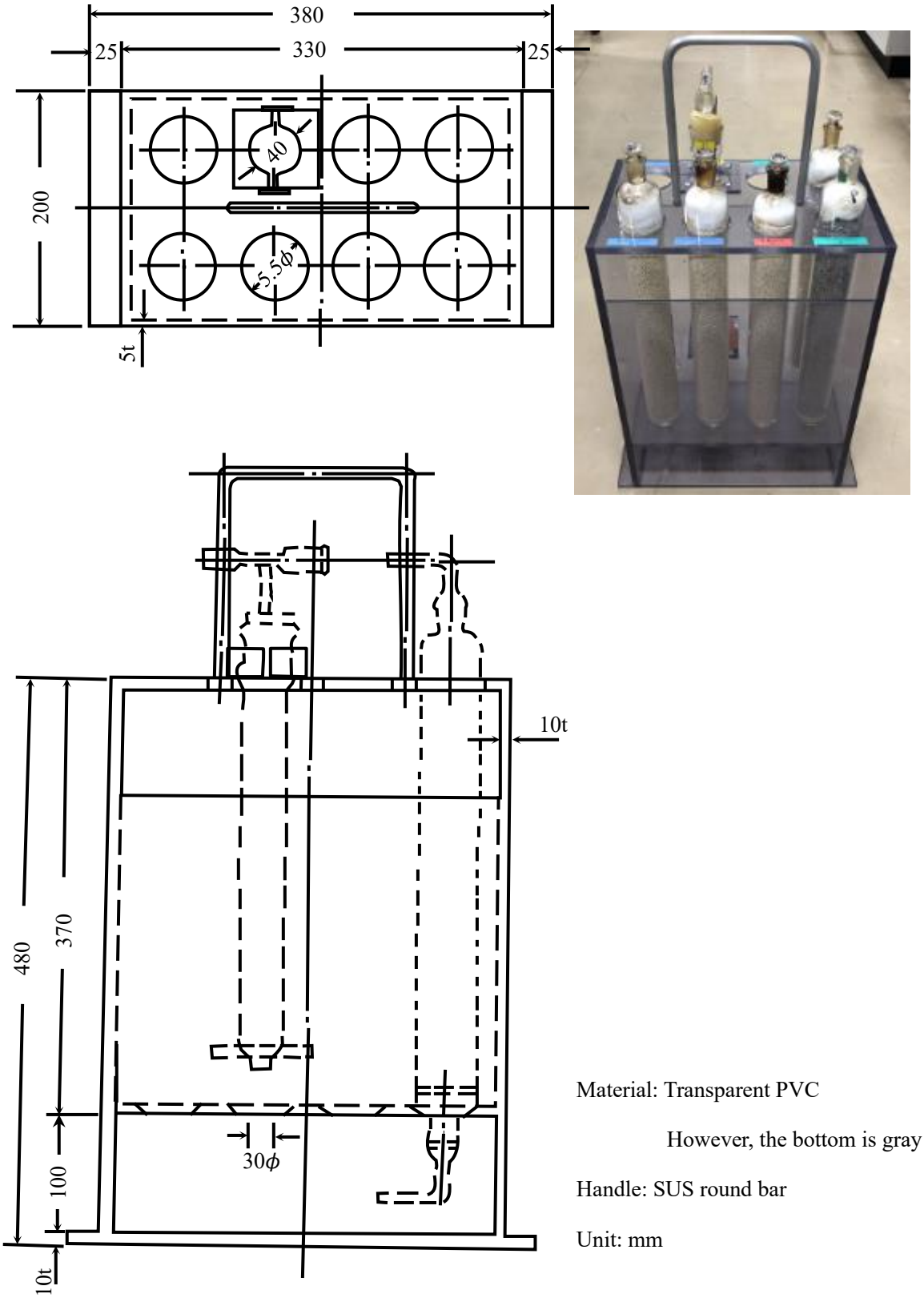


Figure 3.5 Schematic of a column case (Example)

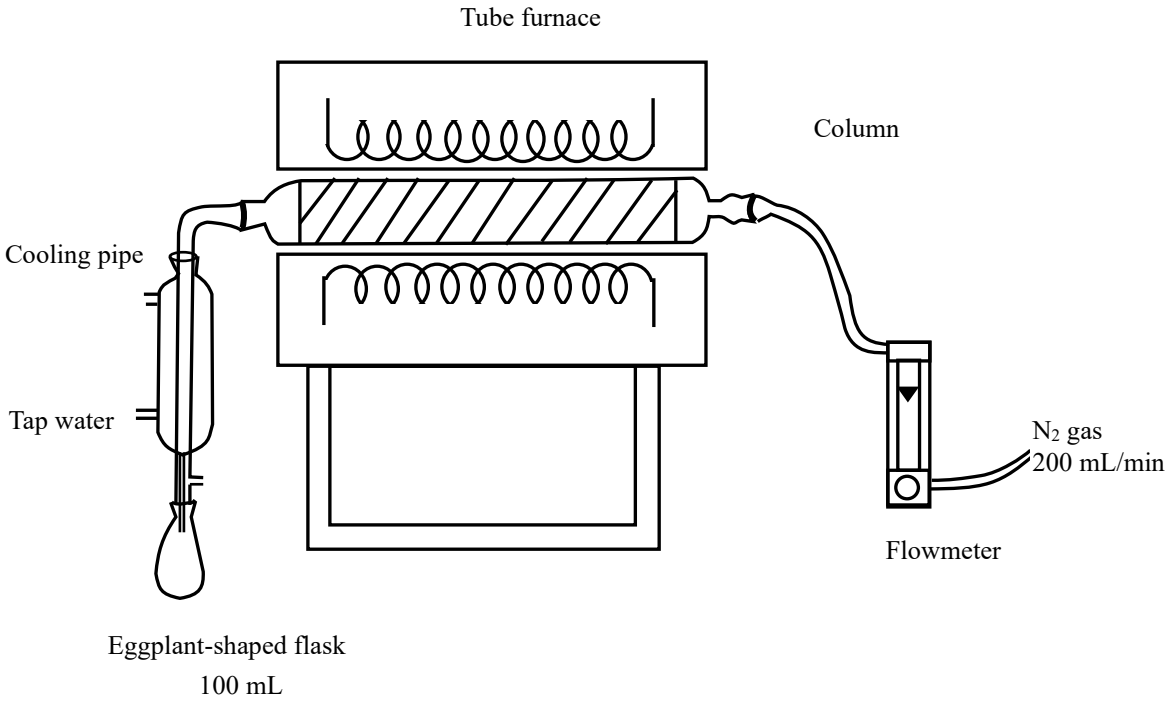


Figure 3.6 Schematic of the baking out of collected water (Example)

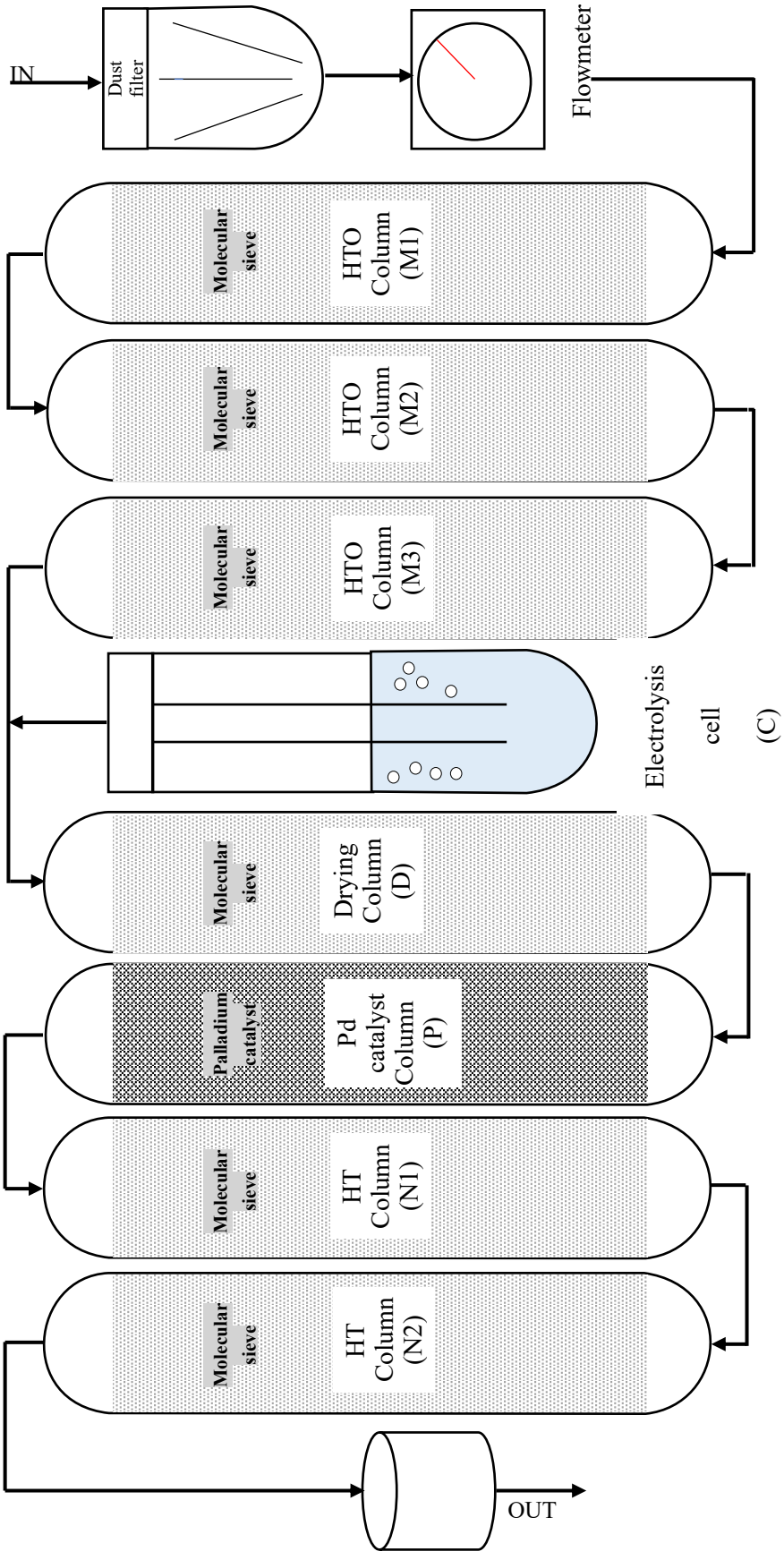
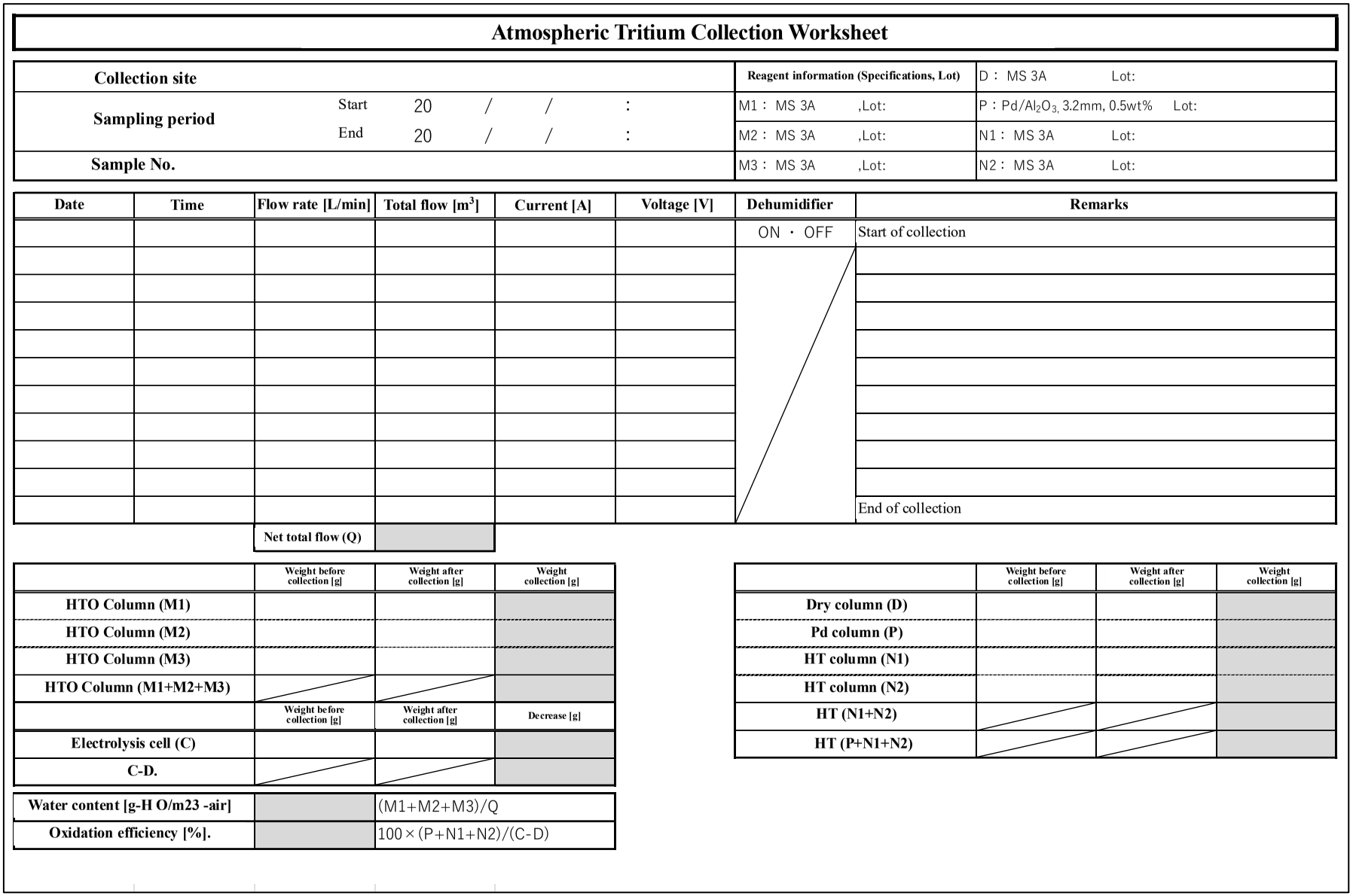


Figure 3.7 Schematic of a system diagram of the HTO and HT collectors (Example)



Atmospheric Tritium Collection Worksheet

Collection site			**Reagent information (Specifications, Lot)**	D： MS 3A Lot:	
Sampling period	Start	20 / / :	M1： MS 3A ,Lot:	P：Pd/Al_2O_3, 3.2mm, 0.5wt% Lot:	
	End	20 / / :	M2： MS 3A ,Lot:	N1： MS 3A Lot:	
Sample No.			M3： MS 3A ,Lot:	N2： MS 3A Lot:	

Date	Time	Flow rate [L/min]	Total flow [m^3]	Current [A]	Voltage [V]	Dehumidifier	Remarks
						ON ・ OFF	Start of collection
		Net total flow (Q)					End of collection

	Weight before collection [g]	Weight after collection [g]	Weight collection [g]
HTO Column (M1)			
HTO Column (M2)			
HTO Column (M3)			
HTO Column (M1+M2+M3)			
	Weight before collection [g]	**Weight after collection [g]**	**Decrease [g]**
Electrolysis cell (C)			
C-D.			

Water content [g-H O/m23 -air]		(M1+M2+M3)/Q
Oxidation efficiency [%].		100×(P+N1+N2)/(C-D)

	Weight before collection [g]	Weight after collection [g]	Weight collection [g]
Dry column (D)			
Pd column (P)			
HT column (N1)			
HT column (N2)			
HT (N1+N2)			
HT (P+N1+N2)			

Figure 3.8 Example of a tritium collection record form

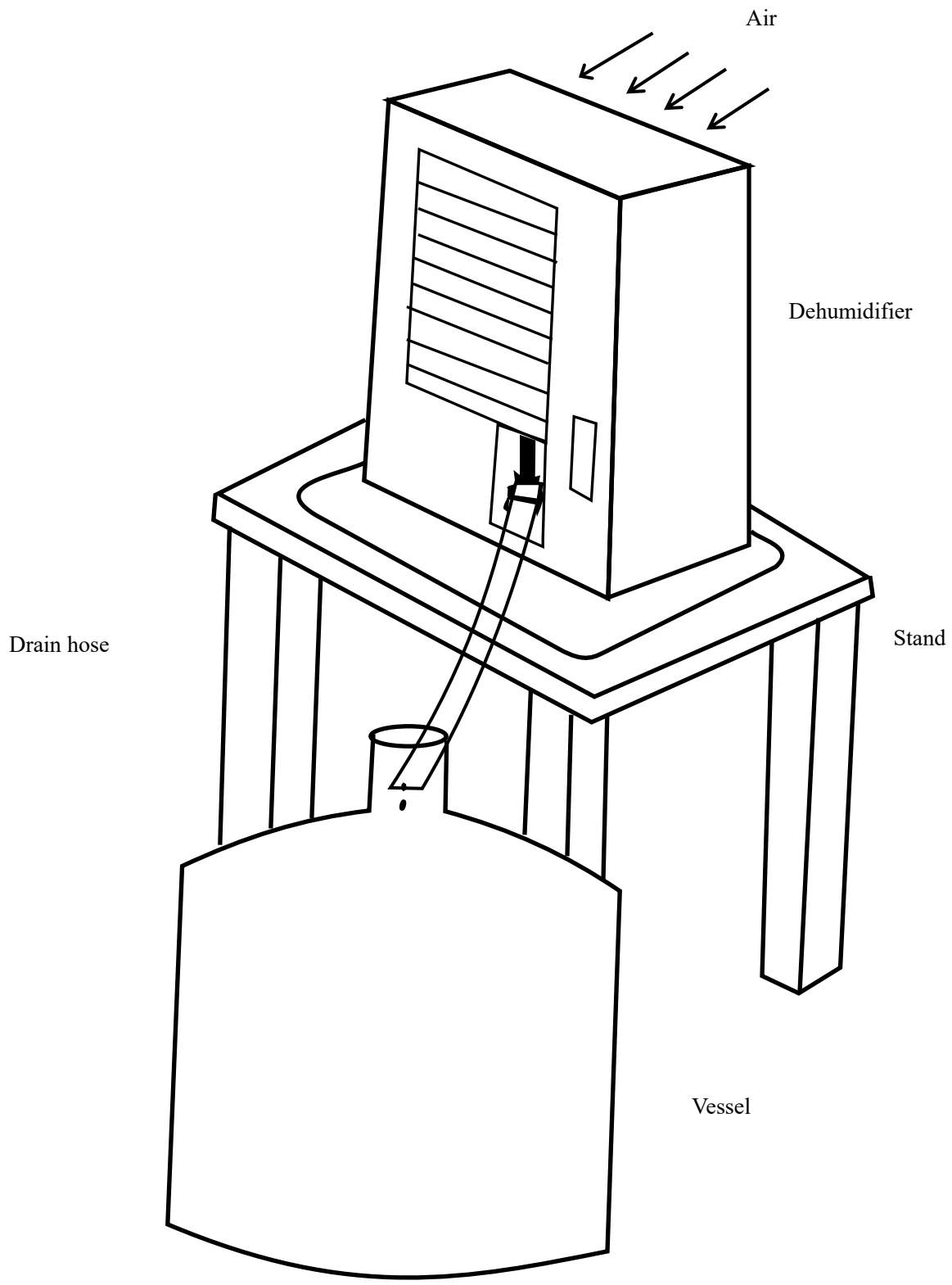


Figure 3.9 Example of water vapor collection using a dehumidifier

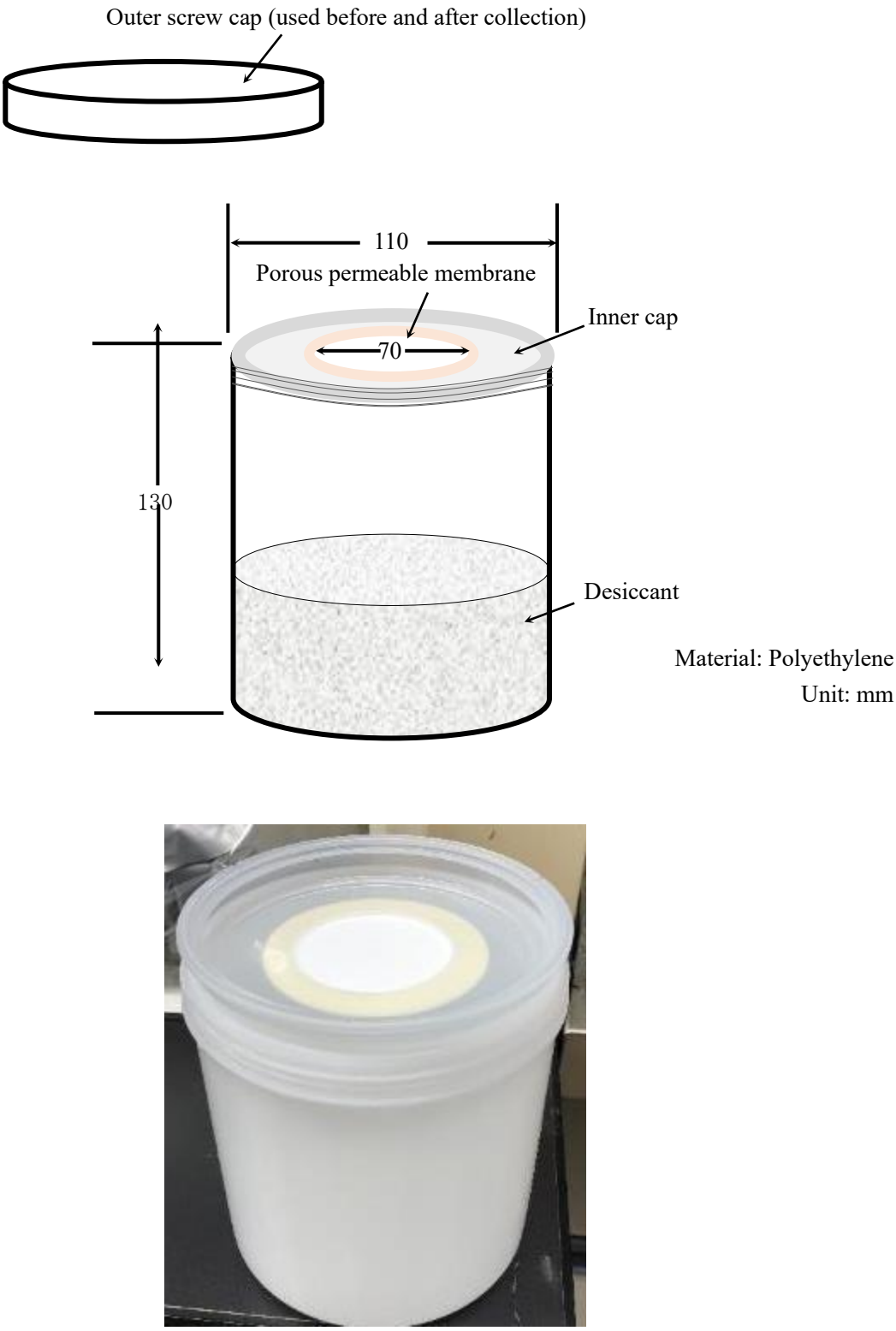


Figure 3.10 Example of the collection vessel for the passive method

Chapter 4 Biological Samples

Biological samples such as rice, fish meat, and pine needles are analyzed primarily for tissue-free water tritium (TFWT). Organically bound tritium (OBT) does not necessarily need to be analyzed at the same time, but it may be analyzed if necessary. Nonexchangeable OBT is describe in Information C because its excretion rate from the body differs from that of the other chemical forms of tritium; additionally, it may be distinguished from exchangeable OBT for dose evaluation.

TFWT is tritium contained in water, which is recovered by the vacuum freeze-drying method[64] and measured after distillation and purification. OBT is tritium contained in water, recovered by the combustion of a sample that has been previously dried and made tissue-free, and is similarly measured after distillation and purification. For evaluating TFWT and OBT without distinguishing between them, such as for screening purposes, a simple method[65] is available, in which water containing mixed OBT and TFWT is collected without vacuum freeze drying.

Purification of sample water via wet decomposition and distillation is an important step in the preparation of the measurement sample.

4.1 Sampling

4.1.1 Sampling location and frequency[66]

(1) Sampling location

In principle, sampling locations shall be set according to the purpose of the survey. When determining sampling locations from the perspective of environmental monitoring around nuclear facilities, it is desirable to consider the environmental conditions around the facility. In addition, setting comparison points that can serve as background data will be helpful when evaluating data.

(2) Sampling frequency

Samples should be collected 1–4 times per year.

4.1.2 Precautions for sample collection

(1) Sample volume

When only TFWT is analyzed, the amount of the sample to be collected is determined by considering the water content[67] of target biological samples. If OBT is also analyzed, the amount

---

[64] Vacuum freeze drying is a method in which a substance or an aqueous solution containing water is rapidly frozen at a temperature below the freezing point, and the frozen material is then depressurized below the water vapor pressure to sublimate water and dry it. Because drying is performed at low temperatures, decomposition and alteration due to heat decreases, along with sample boiling and foaming.

[65] A raw sample is dried/burned in a quartz tube to collect the OBT and TFWT water mixture. In this case, vacuum freeze drying is no longer necessary, which considerably reduces the analysis time; however, this method does not allow the separate evaluation of OBT and TFWT. For more information, refer to the following study. T. Tamari, N. Shima, N. Momoshima, (Secondary Publication) Rapid Tritium Analysis Method in Seafood Dose Evaluation, Jpn. J. Health Phy., 59(2), 88~94 (2024).

[66] This description is an example. When establishing the monitoring plan, refer to the NRA Guideline for Emergency Preparedness and Response and its supplementary reference materials “Ordinary Monitoring” and “Emergency Monitoring.”

[67] If there are no actual measurements of the water content in biological samples, refer to the following documents.

of water obtained by the combustion of a dry sample is determined to obtain at least 70 mL water because the amount of water obtained via combustion is equivalent to 50%–60% of the dry mass.

(2) Sample storage

It is recommended to freeze and store biological samples (raw) immediately after collection by performing the following steps 1) – 3), and then conduct vacuum freeze drying as described in 4.2 Recovery of tissue-free water by the vacuum freeze-drying method. However, if the sample` cannot be processed immediately after collection, it is recommended to freeze the sample immediately after collection and store it at the freezing temperature until analysis to prevent the oxidative degradation of organic matter in the sample by microorganisms.

1) Extract the target part from the sample. For a fish sample, cut it into three or five thin slices, remove head, bones, viscera, fins, scales, skin, etc., and take edible parts as analysis samples. Shred edible parts into cubes of size 1–2 cm. It is desirable to remove the skin because it is difficult to match the sizes of skin and muscle particles when grinding dried materials for OBT estimation due to their different properties. For a shellfish sample, shuck and take meat. For a vegetable sample, remove roots and core, peel, and cut into appropriate sizes. For pine needles, wormwood, etc., shred them.

Shredding is needed because if the material is frozen in large chunks, the inside of the chunks may melt during the vacuum freeze-drying process.

2) After processing the raw sample, seal the sample in a thick plastic bag to prevent moisture in air from adhering to the sample and moisture in the sample from escaping due to drying. Further, seal the bag in a double-layer plastic bag, and immediately freeze the sample. Because water in the environment may condense during freezing, it is recommended to use aluminum-coated bags with moisture-proof and gas-barrier properties or utilize a vacuum sealer to remove air from the bag before sealing.

The vacuum freeze-drying time can be reduced using a large number of bags and freezing in small portions. (See Explanation C, Study on the Vacuum Freeze Drying of Biological Samples.)

3) Sample records

Refer to the Radioactivity Measurement Methods Series No. 16 "Method for sampling of Environmental Materials" and No. 35 "Generic Procedures for Environmental Sampling in Emergencies."

4) Contamination from high-concentration tritium samples and other sources.

Tritium concentrations in environmental samples are extremely low, while samples from the working environment in nuclear facilities usually have much higher tritium concentrations. Therefore, when samples with extremely different tritium concentrations coexist, care must be taken to prevent contamination to low-concentration ones.

Additionally, attention should be paid to the workers' wristwatches[68].

・16) 日本食品標準成分表 2020 年版（八訂）：文部科学省 科学技術・学術政策局政策課資源室 (https://www.mext.go.jp/a_menu/syokuhinseibun/mext_01110.html)

・平宏和：食品図鑑,女子栄養大学出版部(2006).

[68] There are reports of biological samples being contaminated by tritium leaking from foreign-made radioluminous watches. There is a concern that tritium from wristwatches may migrate into the worker's body and contaminate samples. As with sampling, care must be taken during pretreatment.

4.2 Recovery of tissue-free water by the vacuum freeze-drying method

After separating target parts for analysis, freeze them in a freezer. Water (tissue-free water) is extracted from the frozen sample via vacuum drying and used as the analysis sample. An example of a vacuum freeze dryer is shown in Figure 4.1.

1) The trap section in the vacuum freeze dryer and inside of the drain hose must be cleaned in advance.
2) Weigh the frozen sample in a stainless steel drying container whose weight has been measured beforehand. The net weight is obtained by subtracting the container weight.
3) Set the drying container with the frozen sample in the vacuum freeze dryer, and start vacuum freeze drying. Check for leaks in the vacuum system, and note the pressure in the system.
4) Perform vacuum freeze drying until the sample weight becomes almost constant. Record weight changes during drying once per day, if necessary. The time required for achieving a constant weight can be reduced by increasing the surface area of the frozen sample, such as by dividing it into small portions; however, care shall be taken with polished rice, especially brown rice, as achieving its constant weight is difficult.
5) Melt the surface of the ice sample collected in a cold trap attached to the trap, and collect the sample.
6) Transfer the collected water sample to a container whose weight is measured in advance, measure the weight of the sample, and use it as the TFWT analysis sample[69].
7) Measure the weight of the dried material, and calculate the percentage of dry residue (%).
8) Crush the dried material, and seal it in a double-layer plastic bag or the like to use it as an analysis sample for OBT. It is recommended to use aluminum-coated bags with moisture-proof and gas-barrier properties or utilize a vacuum sealer to remove air from the bag before sealing. If the dried sample after vacuum freeze drying cannot be burned immediately, it shall be stored at freezing temperatures to prevent the oxidative degradation of organic matter in the sample by microorganisms.

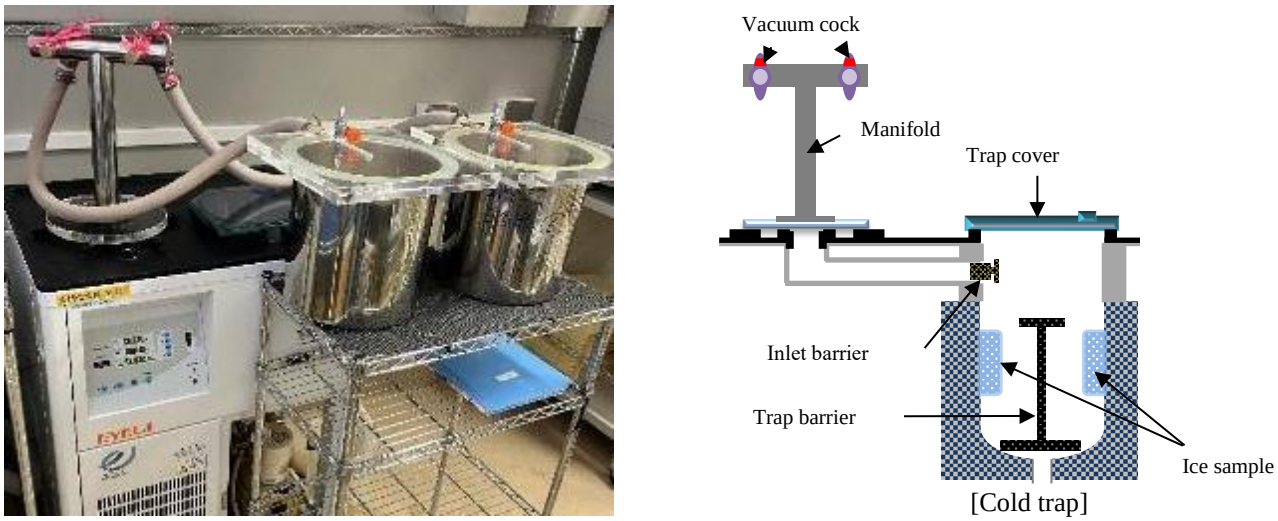


Figure 4.1 Example of a vacuum freeze dryer

[69] In commercially available vacuum freeze dryers, some water vapor is not collected in the cold trap but is exhausted through the vacuum pump. Therefore, the quantitative recovery of tissue-free water is not possible, and a loss of up to 5% is expected.

4.3 Recovery of combustion-generated water

This section describes methods used for burning vacuum freeze-dried materials and recovering generated moisture (combustion-generated water).

There are two methods for this purpose: (i) arrange samples in a quartz tube and burn them in a mixed stream of nitrogen and oxygen using a tube furnace and (ii) burn samples quickly in oxygen gas under high pressure using a commercially available rapid sample combustion device. In this section, combustion methods that use a tube furnace is described. Refer to the instruction manual for instructions on using commercially available equipment.

4.3.1 Combustion method

The following equipment, laboratory instruments, reagents, and gases are required for this method.

(1) Apparatus
- A double-tubular electric furnace (Figure 4.2)
  Dimensions: a mobile furnace with a width of 100 mm and a fixed furnace with a width of 230 mm

(2) Laboratory equipment
- Quartz tube with an inner tube (a length of 400 mm and a diameter of 30 mm) and an outer tube (a length of 900 mm and a diameter of 40 mm)
- Quartz adapter, quartz wool, and hose for gas
- Traps for combustion-generated water (two types), a Dewar bottle, a 1 L beaker, and a flowmeter
- A 100 mL eggplant-shaped flask

(3) Reagents and gases
- Copper oxide (needle-shaped)
- Oxygen gas (purity 99.999%)
- Nitrogen gas (purity 99.999%)

(4) Procedure

1) Fill the outer quartz tube with approximately 250 g copper oxide, and fill both ends with quartz wool to secure copper oxide[70].
2) Plug a small amount of quartz wool into one end of the cleaned and dried inner quartz tube, and measure the tare weight.
3) Fill the inner tube from Step 2 with approximately 50 g sample, and weigh.
4) Plug quartz wool into the opposite side of the tube from Step 2, and set it inside the outer quartz tube.
5) Install the adapter on the intake side, and fix it to the inner and outer tubes.
6) Install the adapter on the exhaust side.
7) Switch ON the combustion unit.
8) Open the oxygen and nitrogen gas valves, and flow both gases at 50 mL/min each into the inner tube and oxygen gas at 100 mL/min into the outer tube.
9) Switch ON the fixed furnace, set the temperature to 650°C–700°C, and start heating[71].

[70]Copper oxide is added to improve combustion.
[71]At room temperature, copper oxide does not have an oxidizing effect on the sample.

10) When the temperature of the fixed furnace reaches 700°C, install the trap for collecting combustion-generated water[72] and flowmeter.
11) Fill the Dewar bottle and 1 L beaker with ice water to cool the trap.
12) Switch ON the mobile furnace, set the temperature to 650°C, and slowly increase the temperature.
13) Once the temperature of the mobile furnace reaches 650°C, open the furnace occasionally and move the mobile furnace gradually while monitoring combustion[73,74,75].
14) Once the mobile furnace has been moved to the fixed furnace, the temperature of the mobile furnace is increased to 700°C to completely burn off any remaining residues and tar adhering to the quartz tube.
15) Moisture adhering to the quartz wool or exhaust side adapter is drawn into the trap by moving the fixed furnace or by heating with a dryer.
16) Once combustion is completed, turn off the oxygen supply to the inner and outer tubes and increase the nitrogen flow rate, allowing only nitrogen to flow for several minutes.
17) Remove the trap, measure the weight, and subtract the tare weight to calculate the weight of combustion-generated water.
18) Depending on the amount of combustion-generated water collected, repeat Steps 2–4 several times[76].
19) Purify collected combustion-generated water according to 4.4 Purification of sample water, and then use it as the measurement sample.
20) Close the oxygen and nitrogen gas valves, and switch OFF the mobile and fixed furnaces.
21) Turn OFF the combustion equipment.

[72] Measure the tare weight of the trap in advance.
[73] If it moves too fast, it will cause rapid combustion, and the flowmeter will swing over the limit.
[74] In the latter half of combustion, tar adheres to the quartz tube and the gas flow becomes sluggish; therefore, move the furnace even more slowly.
[75] If rapid combustion occurs, move the mobile furnace away from the combustion zone temporarily, stop the oxygen supply, and increase the nitrogen gas flow.
[76] Depending on the sample, combustion-generated water equivalent to approximately 50% – 60% of the amount of the dry material used for combustion can be recovered; therefore, to obtain 50–70 g combustion-generated water, 2–3 combustion operations must be performed.

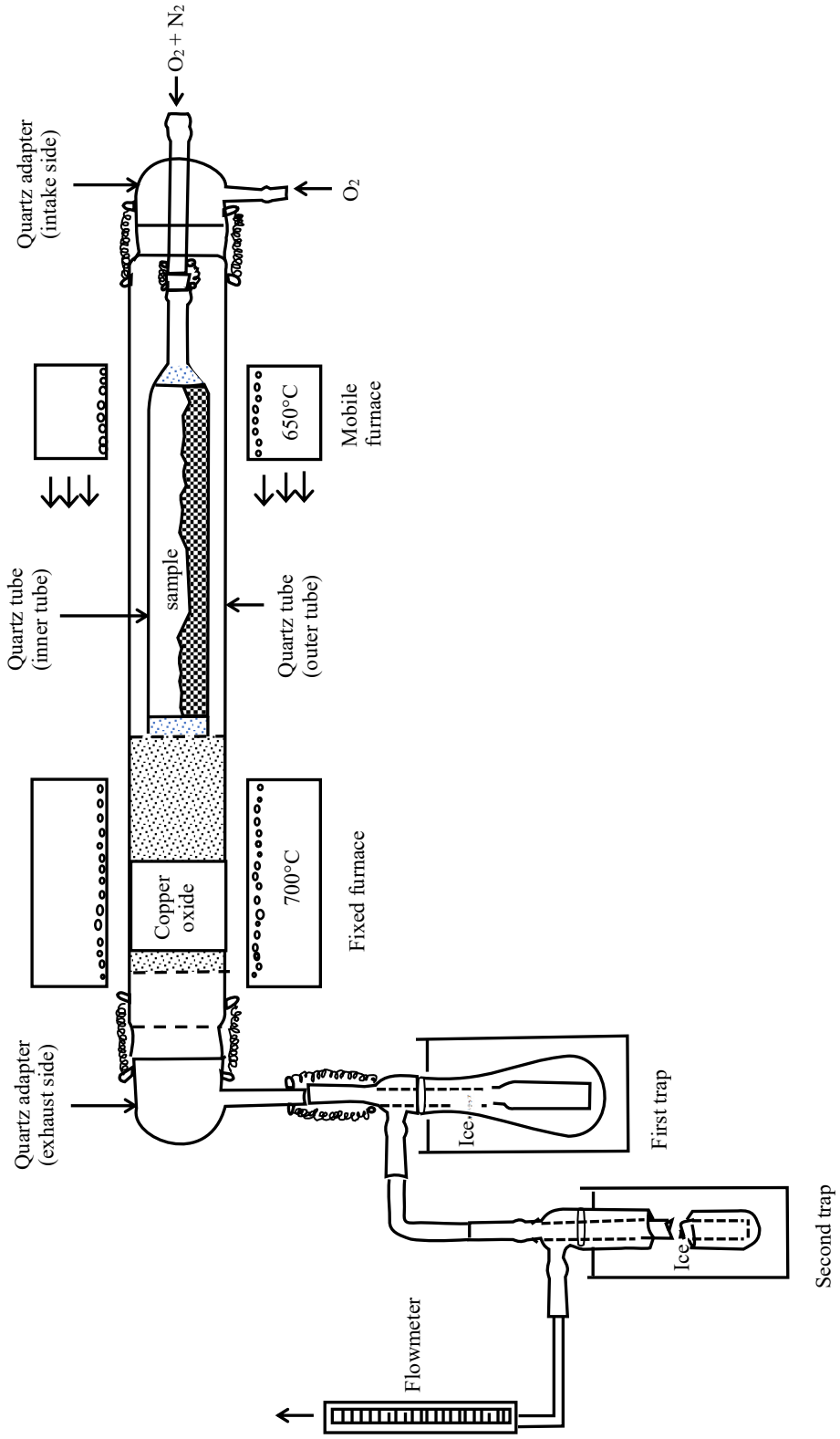


Figure 4.2 Example of a sample combustion apparatus for OBT analysis

4.3.2 Rapid combustion method

The method involves the rapid combustion of biological samples (rice, vegetables, milk, etc.) that have undergone freeze vacuum drying using a commercially available rapid sample combustion device to obtain combustion-generated water, which is collected in a cold trap in a vacuum line.

The amount of sample that can be burned in one combustion operation is ~30 g for polished rice and ~20 g for pine needles, fish meat, and milk powder samples. The sample amount is limited by the specific gravity of each sample and capacity of the metal container for combustion.

The following equipment, laboratory instruments, reagents, and gases are required for this method.

(1) Apparatus
- A commercial rapid sample combustion device (Figure 4.3)
- A vacuum line (Figure 4.4)

(2) Laboratory equipment
- Water bath

(3) Reagents and gases
- Silica gel
- Cooling materials such as liquid nitrogen or dry ice–acetone
- Oxygen gas (purity 99.999%)

(4) Procedure

1) Dispense 20–30 g analysis sample into a sample combustion container, and weigh.
2) Connect an ignition fuse (with a length of 10 cm) between the terminals, and set it in such a way that the fuse lightly touches the sample.
3) Inspect the O-ring in the sample combustion device, and set it in place.
4) Securely attach the lid of the sample combustion device with the mounting bracket.
5) Fill the sample combustion device with oxygen gas up to 20 kg/cm^2 using a dedicated regulator and a gas filler.
6) When gas filling is completed, close the valve on the gas-filling side of the sample combustion device and gauge valve, and remove the gas filler.
7) Connect one end of the ignition cable to the ignition terminal of the sample combustion device and the other end to the ignition device, and press the ignition switch to burn the sample. Ensure that the top of the device becomes hot.
8) Wait for the sample combustion device to cool down, and then further cool the lower part of the combustion device sufficiently with ice.
9) Slowly open the exhaust valve to exhaust oxygen and carbon dioxide produced during combustion until the inside of the device almost reaches the atmospheric pressure.
10) Connect the connection joint to the exhaust valve, and then connect the connection joint to the vacuum line.
11) After heating the lower part of the combustion device in a water bath at~70°C and cooling the cold trap with a cooling material, open the exhaust valve of the device very slowly to collect water vapor in the cold trap.
12) After 2–3 h of continuous collection, temporarily close all valves at once.
13) Remove the cooling material from the trap, and slowly open the valve A to release vacuum.
14) Remove the cold trap, and measure the weight. Subtract the premeasured tare weight to obtain the weight of recovered water.

15) Purify collected combustion-generated water according to 4.4 Purification of sample water, and then use it as the measurement sample.

16) After combustion, the sample combustion container may contain carbide or other substances adhere to it, which must be removed by heating it for several minutes using a gas burner or other means[77].

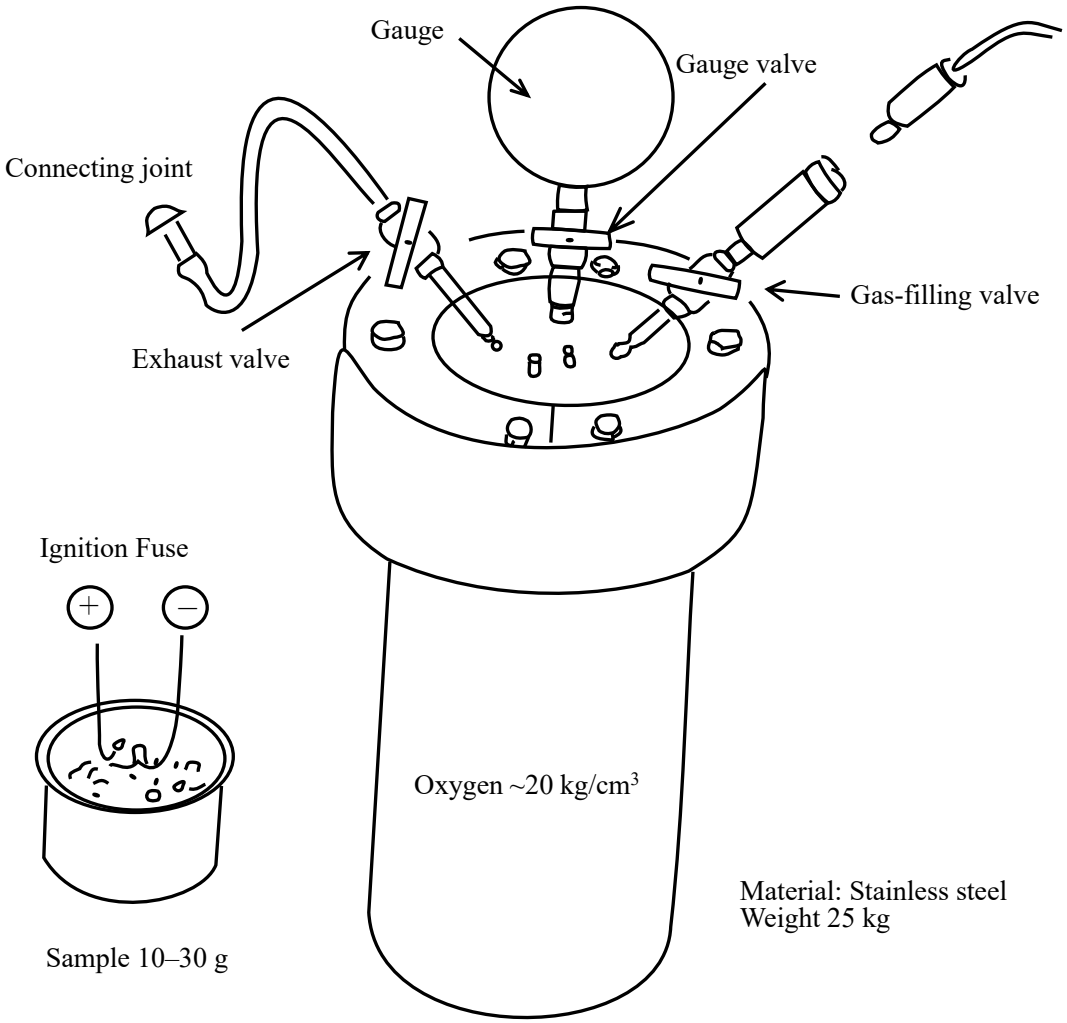


Figure 4.3. A rapid sample combustion device (commercially available)

[77] Even if no visible residues remain, after burning a sample with a high tritium concentration, it is necessary to thoroughly bake out the sample combustion container by heating, considering the memory effect.

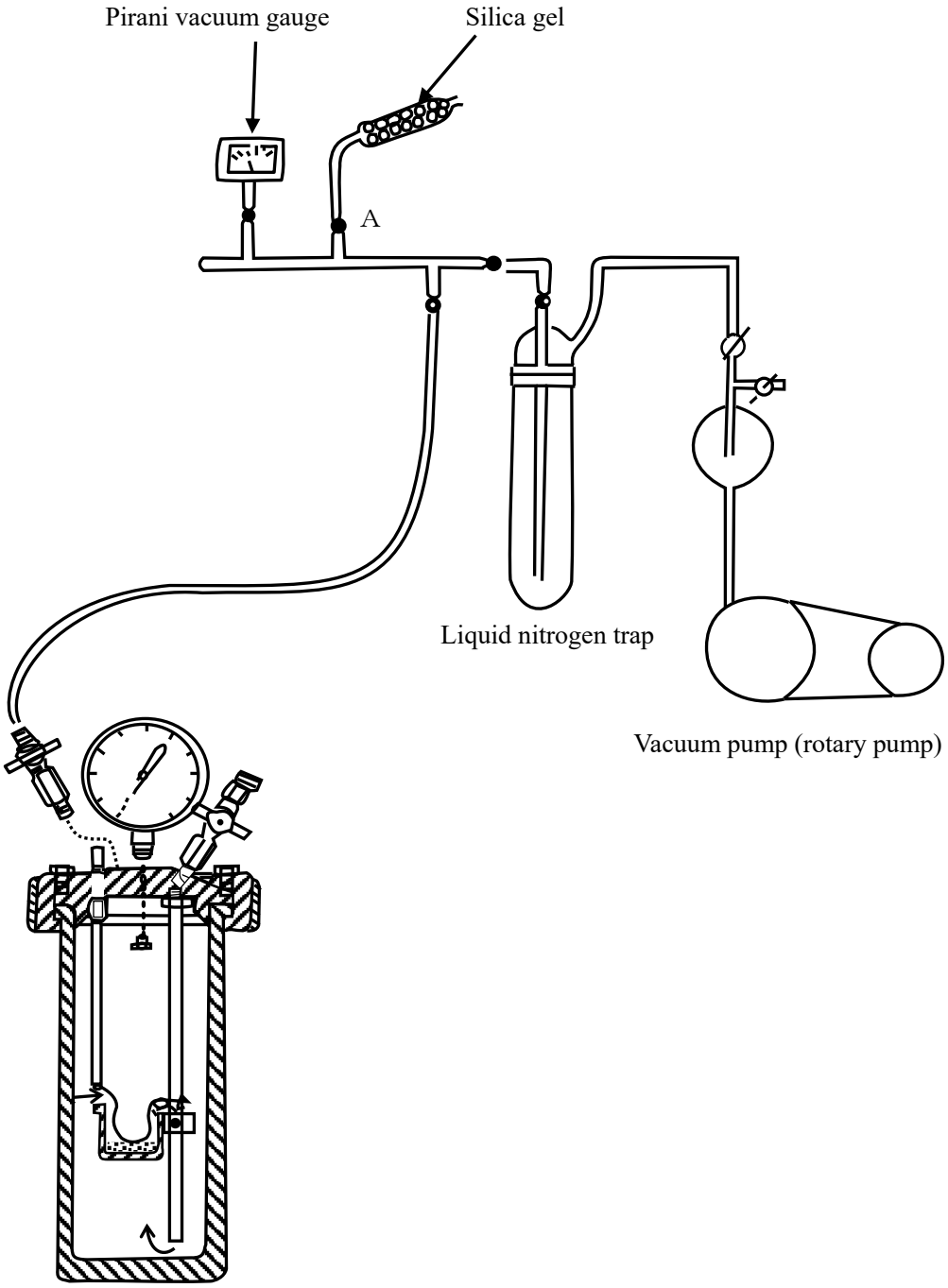


Figure 4.4 Example of a combustion-generated water recovery system

4.4 Purification of sample water

This section presents a method used for the wet decomposition of organic matter in tissue-free water and combustion-generated water by adding an oxidant and refluxing, followed by distillation.

Refluxing can be omitted depending on the amount of organic matter in the sample.

4.4.1 Wet decomposition (reflux)[78]

The following laboratory equipment and reagents are required in this section

(1) Laboratory equipment

- A 100 mL eggplant-shaped flask
- Vinyl tape
- A reducing adapter
- A Dimroth condenser
- Aluminum foil
- Tubes for cooling water
- Mantle heater (100 W)
- A voltage regulator (not required if built into the mantle heater)
- A Stand

A schematic of the reflux system is shown in Figure 4.5.

(2) Reagents

- Potassium permanganate ($KMnO_4$): JIS reagent special grade
- Boiling stones
- Silica gel

(3) Procedure

1) Glassware shall be thoroughly dried beforehand.
2) Add approximately 0.5 g potassium permanganate to an eggplant-shaped flask[79].
3) Add approximately 70 mL analysis sample to the eggplant-shaped flask in Step 2, and shake it to thoroughly dissolve potassium permanganate.
4) Add a small amount of boiling stones.
5) Attach the reducing adapter and Dimroth condenser[80] to the eggplant-shaped flask, and secure it on the stand.
6) Place the mantle heater at the bottom of the eggplant-shaped flask, and connect it to the voltage regulator.
7) Turn ON cooling water, set the voltage regulator to 65 V, and start reflux.
8) Wrap aluminum foil around the flask at the top of the mantle heater to keep it warm.
9) Reflux for at least 4 h.
10) If the color (reddish purple) of potassium permanganate does not remain, the amount added is likely insufficient, so add more, and repeat steps 5–9.
11) After completing reflux, seal the eggplant-shaped flask tightly, and allow it to stand overnight.

---

[78] Refluxing can be omitted depending on the amount of organic matter in the sample.

[79] Adjust the added amount according to the organic content in the sample. In the case of water generated from the combustion of fish samples, approximately 3–5 times more than that used normally shall be added.

[80] A column packed with silica gel is mounted at the upper port of the Dimroth condenser to prevent water vapor from entering from outside.

4.4.2 Distillation of refluxed sample

Distillation is basically the same as that described in 2.2.1 Atmospheric Distillation Method, but the purpose of distillation here is to remove flame-resistant organic matter resulting from incomplete combustion.

The following laboratory equipment and reagents are required in this section

(1) Laboratory equipment

- A glass rod
- pH test paper
- A Liebig condenser
- An L-shaped tube
- A trap ball
- A 100 mL eggplant-shaped flask
- Aluminum foil
- Mantle heater (100 W)
- A Stand
- Tubes for cooling water
- A voltage regulator (not required if incorporated in the mantle heater)
- Connecting clips

A schematic of the small distillation unit is shown in Figure 4.6. The small distillation unit is used to minimize losses during the distillation of combustion-generated water.

(2) Reagents

- Sodium peroxide (Na_2O_2): granular (≥95% purity)
- Boiling stones

(3) Procedure

1) While cooling the eggplant-shaped flask in an ice bath, add sodium peroxide to neutralize the sample. Add a small amount more of sodium peroxide to make the sample alkaline. Check the sample pH with a pH test paper.
2) Fix the Liebig condenser to the stand, attach the L-shaped tube and trap ball[81], and secure with clips.
3) Attach the eggplant-shaped flask (from Step 1) to the port of the trap ball and a washed and dried 100 mL eggplant-shaped flask or a fluoroplastic vial to the L-shaped tube side.
4) Place the mantle heater at the bottom of the eggplant-shaped flask, and connect it to the voltage regulator.
5) Wrap aluminum foil around the mantle heater and L-shaped tube sections[82].
6) Turn ON cooling water, set the voltage regulator to 65 V, and start distillation.
7) Distill until sample becomes dry. After completing distillation, if the distillate shows coloration due to the presence of potassium permanganate, repeat Steps 1–7 again[83,84].

---

[81] Because the refluxed sample contains a large amount of potassium permanganate, potassium permanganate easily gets mixed into distilled water, turning it purple. Incorporate a trap ball to prevent this.

[82] The mantle heater section is wrapped to keep it warm, and the L-shaped tube section is wrapped to prevent dust and other particles from entering.

[83] This is because the color of potassium permanganate often does not disappear after a single atmospheric distillation.

[84] Remember to add boiling stones to the eggplant-shaped flask.

8) Measure the pH and ultraviolet (UV) absorption of the distillate to confirm that it is neutral and does not exhibit a peak at a wavelength of ~200 nm.

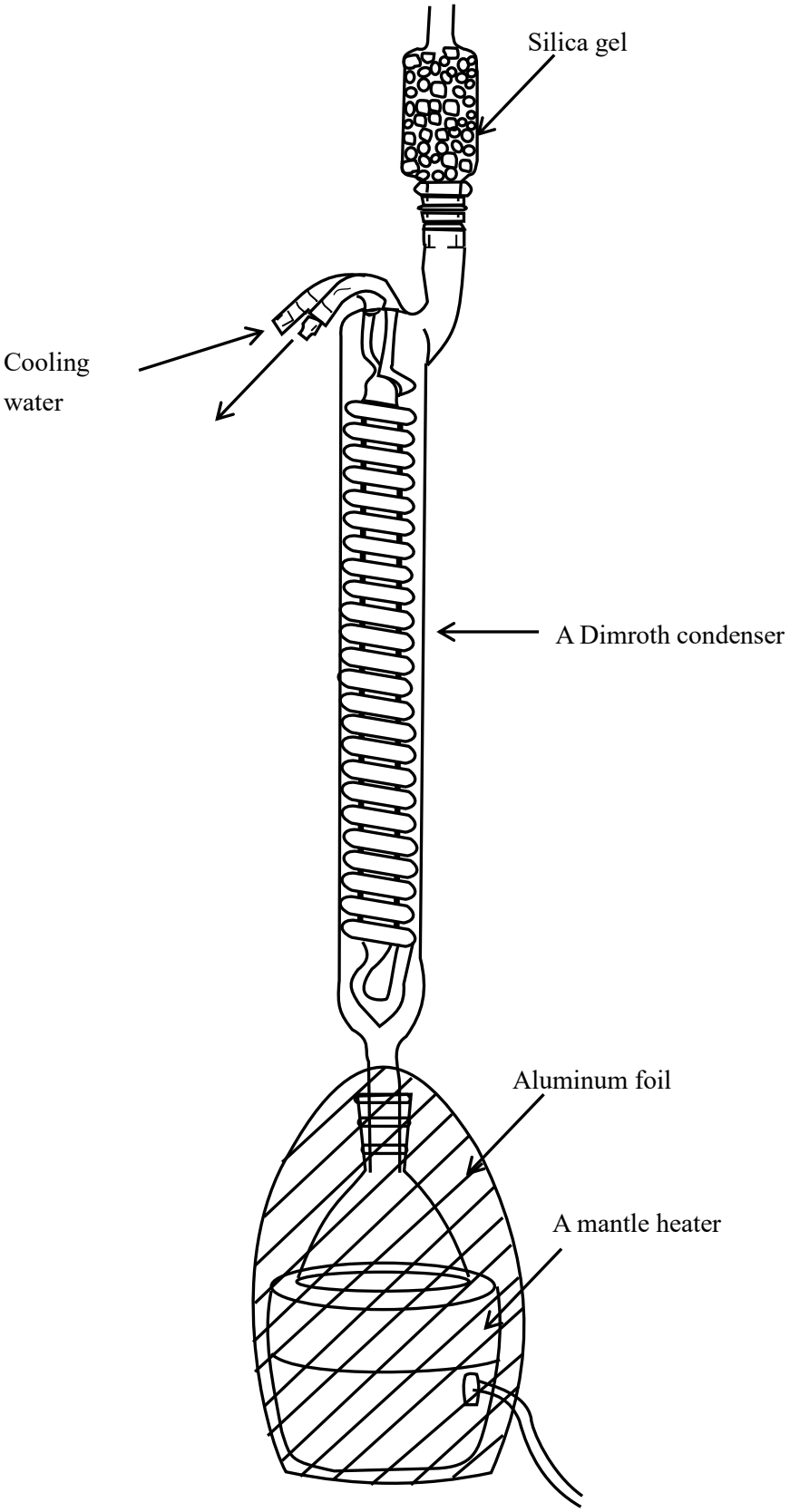


Figure 4.5 Example of a reflux device

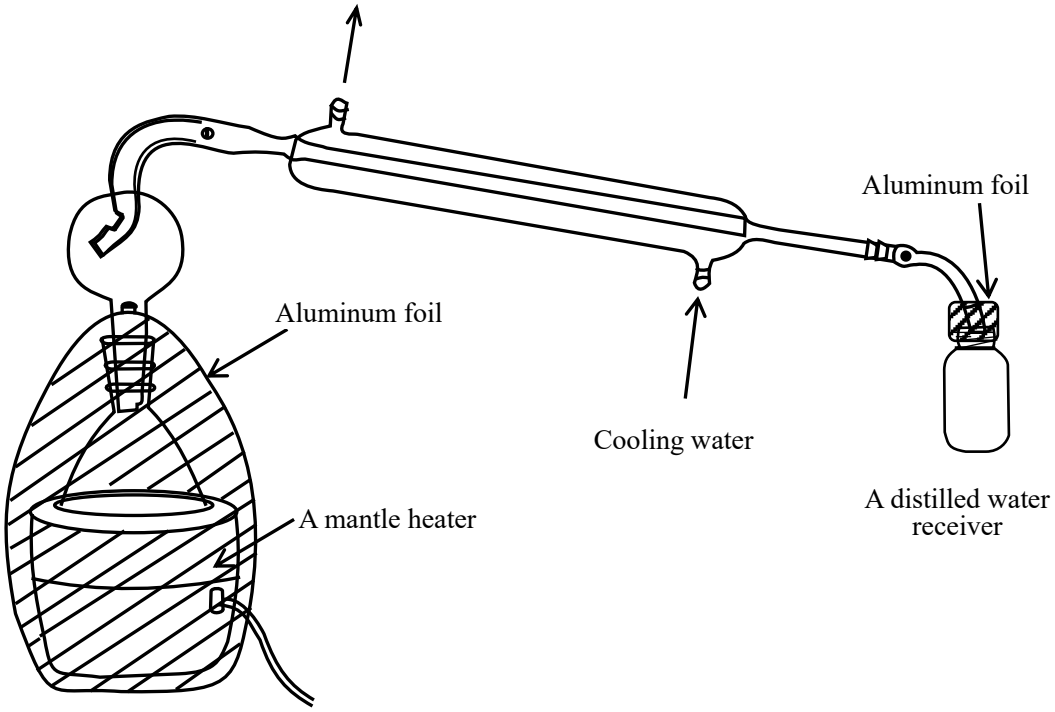


Figure 4.6 Example of a small distillation unit[85]

[85] Use an eggplant-shaped flask or a fluoroplastic vial to collect distilled water. When processing multiple samples simultaneously, ensure that cross-contamination does not occur. In the case of an open system, it is recommended to cover it with aluminum foil. For closed systems, silica-gel tubes shall be installed to avoid pressurized conditions.

Chapter 5 Setting and Calibration of Measurement Conditions

Water samples obtained in Chapters 2, 3, and 4 are mixed with an emulsified scintillator to prepare measurement samples, and the tritium concentration is measured using an LSC. Simultaneously, the amount of light emitted by the emulsified scintillator due to radiation is reduced by the presence of water molecules, which are impurities. The degree of attenuation is called quenching, and it must be corrected using a standard sample. To determine the counting efficiency of the measurement sample, a quenching-correction curve, which is a relationship curve between tritium counting efficiency and the index value of the quenching level, shall be prepared in advance using several standard samples at different quenching levels.

5.1 Preparation of standard samples for quenching-correction curve

Standard samples for creating quenching-correction curves comprise a set of 5–10 samples with different quenching levels. They should be prepared in such a way that matches the actual preparation method of measurement samples and should cover the range of quenching levels expected for measurement samples.

The preparation method by varying the water content is shown below for a 100 mL measuring container. The conditions for preparing measurement samples are determined by the sample retention of the emulsified scintillator used. If a 20 mL measurement vial is used, samples can be prepared by varying the amount of the tritium standard solution and emulsified scintillator added so that the water content is the same in all cases.

5.1.1 Preparation method

The following laboratory equipment and reagents are required in this section

(1) Laboratory equipment
- A total of 5–10 fluoroplastic vials (100 mL, with an inner lid)
- A balance (with a minimum scale of 0.0001 g)
- Graduated cylinders (20 and 50 mL)
- Fixed quantity pipette
- Pipette tip
- Water bath (to be used as needed)

(2) Reagents
- Tritium standard solution (tritium concentration of approximately1×10^3 Bq/g, approx. 10 mL, available from calibration laboratories)
- Emulsified scintillator (commercially available)
- Purified water (not necessarily tritium-free water), tritium-free water

(3) Procedure

1) Measure the weight of the vial with the lid on.

2) Add the tritium standard solution so that the counting rate is greater than 5,000 cpm. As the water content increases, counting efficiency decreases.

3) For example, with a total water volume of 10 mL (tritium standard solution + diluted purified water, the same shall apply hereafter), counting efficiency is approximately 30%, and with a total water volume of 55 mL, counting efficiency is approximately 20%. In this

case, a standard solution with a radioactivity of 1×10^3 Bq/g will require 1–2 g standard solution to achieve more than 5,000 cpm.

4) After taking the standard solution, quickly close the lid, and measure the mass. In this instance, the amount of the standard solution is calculated assuming a specific gravity of 1.
5) Add purified water to each vial to prepare 10-, 20-, 30-, 35-, 40-, 45-, 50-, 52-, and 55-mL solutions in combination with the previously prepared standard solution.
6) Add the emulsified scintillator to each vial to prepare a total volume of 100 mL for each solution. An example of the preparation results is shown in Table 5.1.
7) Cover the measuring container, and shake it gently.
8) If the emulsified scintillator does not require heating, it can be mixed with samples uniformly by simply shaking the measuring container. For emulsified scintillators that require heating, use a water bath to heat the measuring container by immersing it in warm water (~50°C), and mix the mixture by shaking it until it becomes clear. If the scintillator is heated too much, it will emulsify and turn white but will become transparent as it cools. Before use, check the instruction manual for the emulsified scintillator.
9) After sample preparation, leave samples in the instrument or in a cool, dark place for 24 h before measuring their quenching-correction curves[86].

5.2 Background sample preparation

When measuring tritium, the background counting rate due to the emulsified scintillator, measuring container, measuring instrument, etc. must be subtracted from the counting rate of the sample.

Hence, a background sample is prepared using tritium-free water with the same composition (water content) as the sample water for each measurement.

Deep groundwater, deep sea water, and natural-gas combustion water are used as tritium-free water, which must be distilled and purified beforehand.

Tritium-free water to be used shall be accurately analyzed using the electrolytic enrichment method described in this manual (DL level: 60–70 mBq/L) to confirm that no tritium is detected before use.

The following laboratory equipment and reagents are required in this section

(1) Laboratory equipment
- A measurement container (use a container made of fluoroplastic (100 mL), low-potassium glass (20 mL), polyethylene (20 or 145 mL), etc.)
- Water bath (to be used as needed.)

(2) Reagents
- Tritium-free water
- Emulsified scintillator (use a commercially available product. See [Explanation D])

[86] The prepared standard samples should be stored in a cool and dark place, similar to the inside of the analyzer (temperature approximately 15°C). Furthermore, for standard samples that have been stored for a long period of time (six months to a year), the gel state is more likely to become unstable and deteriorate as its water content decreases or increases Ensure that there is no change in the weight or quenching index values before use.

(3) Procedure

1) The amount of tritium-free water is obtained by multiplying the optimum measurement liquid volume, which is determined from the LSC and measuring container used, by the optimum water retention rate of the emulsified scintillator[87].

2) For example, if the emulsified scintillator and a 100 mL measuring container are used, the volume of tritium-free water should be 40–50 mL, and the volume of the emulsified scintillator be 60–50 mL for a total volume of 100 mL. When using a 20 mL measuring container, the volume of tritium-free water shall be 8–10 mL, and the volume of the emulsified scintillator be 12–10 mL for a total volume of 20 mL.

3) Depending on the employed emulsified scintillator, using certain mixing ratios tends to separate the mixture into two phases; therefore, mixing in such ranges should be avoided[88].

4) Measure the precise volume of tritium-free water (specific gravity of water of 1 g/cm^3), and transfer to a measuring container.

5) Accurately add the emulsified scintillator to tritium-free water with an automatic burette or other means, and mix to obtain the optimum measurement liquid volume described in Step 1.

6) Cover the measuring container, and shake it gently.

7) If the scintillator does not require heating, it can be mixed with samples uniformly by simply shaking the measuring container. For scintillators that require heating, use a water bath to heat the measuring container by immersing it in warm water (~50°C), and mix the mixture by shaking it until it becomes clear. If it is heated too much, it will emulsify and turn white but will become transparent as it cools. Before use, check the instruction manual for the emulsified scintillator.

8) After washing the outside of the measuring container with distilled water, wipe-off water, handprints, etc. with paper towels, etc., and place the sample in a cool, dark place to stabilize it (refer to 6.1 Preparation of measurement samples for the duration).

[87] Because the optimum measurement volume varies slightly depending on the employed LSC and measuring container, considering the optimum measurement volume and optimum water retention rate of the emulsified scintillator in advance is necessary if high counting efficiency is desired.
The optimum measurement liquid volume is usually determined so that the value of (counting efficiency) x (measurement liquid volume) becomes maximum.
Similarly, the optimum water retention rate of the emulsified scintillator should be the maximum value of (counting efficiency) x (water retention rate).

[88] Refer to the instruction manual for the emulsified scintillator used.

Table 5.1 Standard sample preparation sheet for tritium efficiency

Total water volume (mL)	100 mL vial (with lid) + HTO (g)	100 mL vial (with lid) (g)	HTO (g)	HTO Radioactivity (Bq)	Value after decay correction for HTO D.F.(Decay Factor) = 0.813386 (date)				Remarks
					HTO radioactivity (Bq)	Counting rate (cpm)	Eff*1 (%)	Quenching index value*2	
10	50.7998	45.7562	5.0436	995.10	809.40	13,990.46	28.81	3.87	
20	50.7625	45.3278	5.0499	996.35	810.41	13,820.98	28.42	3.52	
30	50.3856	45.3278	5.0578	997.90	811.68	13,324.16	27.36	3.14	
40	50.6342	45.5654	5.0688	1,000.07	813.45	12,399.01	25.40	2.77	
45	50.7445	45.6823	5.0622	998.77	812.39	11,726.58	24.06	2.57	
50	50.3546	45.3227	5.0319	992.79	807.52	11,010.81	22.73	2.37	
52	50.8765	45.7997	5.0768	1,001.65	814.73	10,670.21	21.83	2.25	
55	49.5621	45.2914	4.2707	842.61	685.37	8,573.61	20.85	2.13	

Undiluted standard solution concentration for efficiency: 197.3 Bq/g (date: Xth (day), XX (month), 202X(year))

*1 Eff: Efficiency, counting efficiency

*2 Quenching index value: Index value indicating the degree of quenching when an external standard source is used (refer to 5.3.2).

5.3 Setting of measurement conditions

This section describes the setting of the optimum window (equivalent to energy) for tritium concentration measurements and preparation of quenching-correction curves using standard samples for creating the quenching-correction curve prepared in 5.1 Preparation of standard samples for quenching-correction curve and background sample prepared in 5.2 Background sample preparation.

5.3.1 Setting the measurement conditions based on the figure of merit (FOM)

When measuring low-level radioactivity such as that in environmental samples, it is recommended to set the measurement conditions so that uncertainty due to counting statistics is as small as possible. The FOM is used as a guideline here. It is defined as follows:

$$FOM = \frac{E^2}{B}$$

where E (%) is the counting efficiency and B (cpm) denotes the background counting rate. The amplifier gain, lower-level discriminator (LLD), and upper-level discriminator (ULD) are set to maximize this value, and the measurement conditions are such that uncertainty due to counting statistics is minimized as much as possible. LSCs currently available on the market are generally equipped with a built-in multichannel wave-height analyzer, and the generated spectra can be viewed on the screen during measurement.

The following is the procedure for setting the measurement window of the channel for tritium concentration measurement when using the LSC.

(1) Gain setting

No gain setting is required. Gain is automatically set to the optimum gain for tritium measurement.

(2) Measurement window settings (LLD and ULD)

1) Two samples—the standard sample (40%–50% water content), which exhibits the same level of quenching as the sample, and background sample (40%–50% water content)—are placed in the sample changers[89].

2) Set the measurement conditions of the LSC to the channel for tritium measurement[90].

3) Measure the standard sample with 40% or 50% water content for 10 min to several tens of minutes, and check the β-ray spectrum of tritium on the screen (Figure 5.1).

4) On the screen, place the cursor of the ULD at energy, including the whole spectrum, and change the value of the LLD to 0.1, 0.2, 0.3, 0.4, and so on to obtain each counting rate. Divide the counting rate by the amount of tritium added (Bq) in the standard sample to obtain counting efficiency. Plot this efficiency on a linear graph, and find the LLD where counting efficiency$E$(%) begins to decrease, and fix it there.

5) Switch the cursor to the ULD, move it sequentially from 1.5 to 10.0 keV, with 0.5 keV steps[91], and record each integrated count between the LLD and ULD to obtain the counting rate (cpm).

---

[89] This should be done at least 1 h prior to the start of measurement. This is required to avoid the influence of static electricity on the measurement vial and to maintain a constant sample temperature.

[90] Refer to the instruction manual of the measuring instrument used.

[91] The ULD may be moved even more finely with 0.2 keV steps.

6) Divide the counting rate obtained in Step 5 by the amount of tritium added to the standard sample (Bq) to obtain counting efficiency$E$ (%).

7) Plot the change in the counting efficiency against the ULD on a linear graph (Figure 5.2).

8) Remove the standard sample with 40%–50% water content from the detector, place the background sample prepared with the same water content in the detector, and perform measurement for 900 min Check the background spectrum on the screen (Figure 5.1).

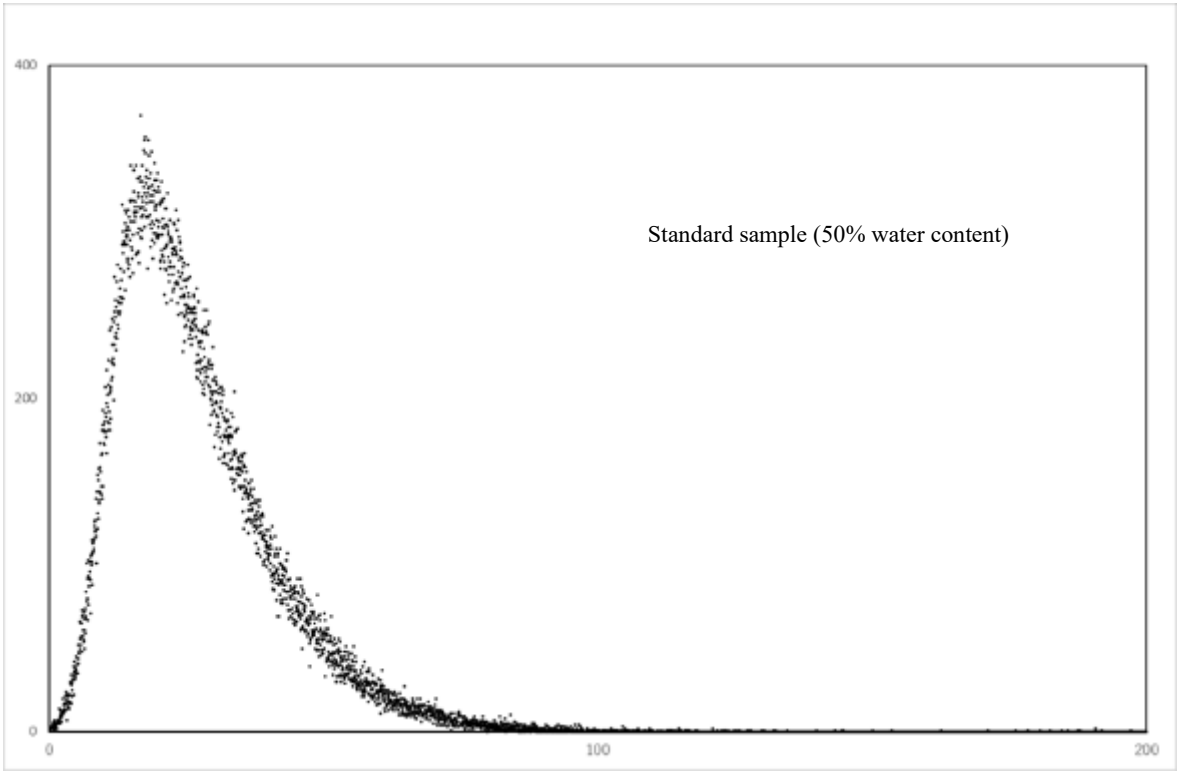
9) Fix the LLD set in Step 4, change the ULD as shown in Step 5, and create a graph of the change in the background counting rate$B$ (cpm) against the ULD (Figure 5.2).

10) Read the background counting rate$B$ (cpm) against the ULD from the graph, and calculate the FOM value.

$$FOM = \frac{E^2}{B}$$

11) Plot the change in the FOM versus the ULD on a linear graph, and set this value to the ULD that maximizes this value (Figure 5.2).

For models with an automatic optimum window determination function, the optimum window setting by the above operation can be automated. Refer to the instruction manual of the employed LSC for operating instructions.



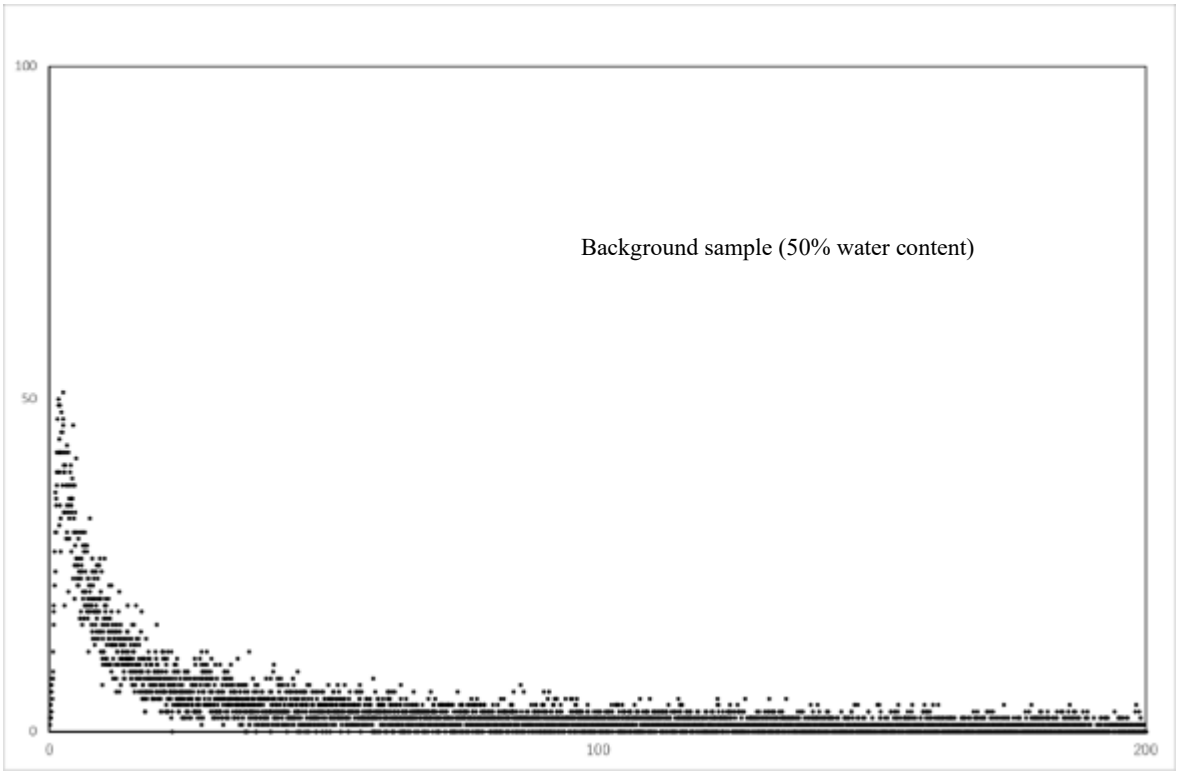
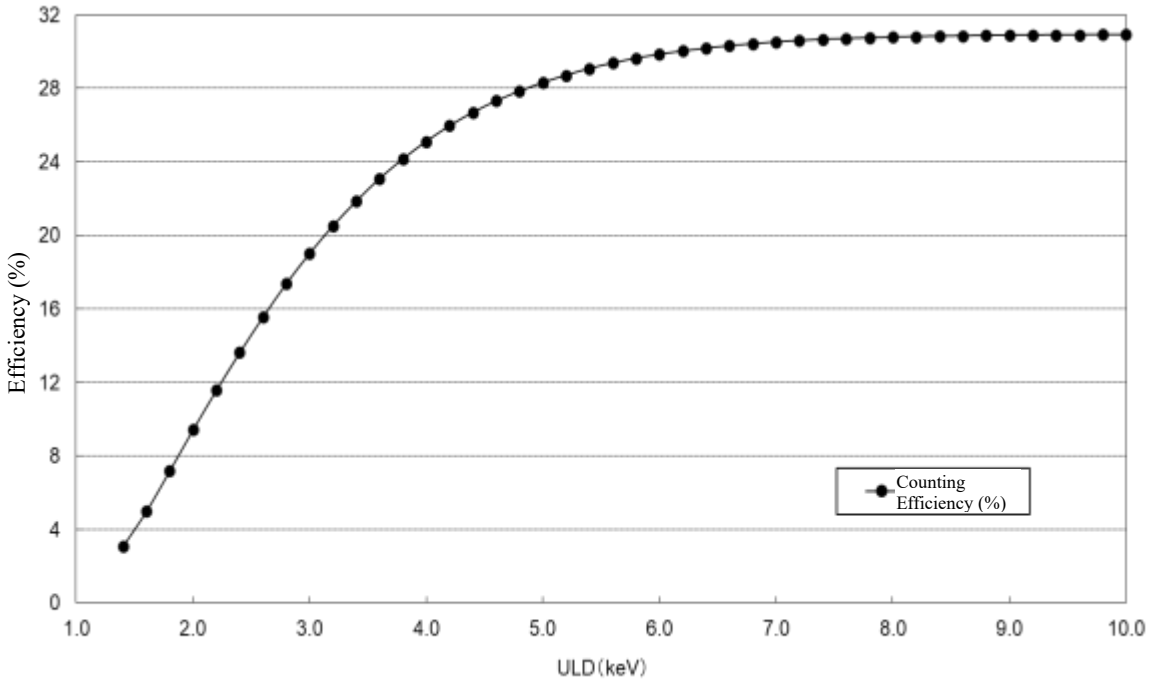


Figure 5.1 Examples of spectra of tritium standard and background samples



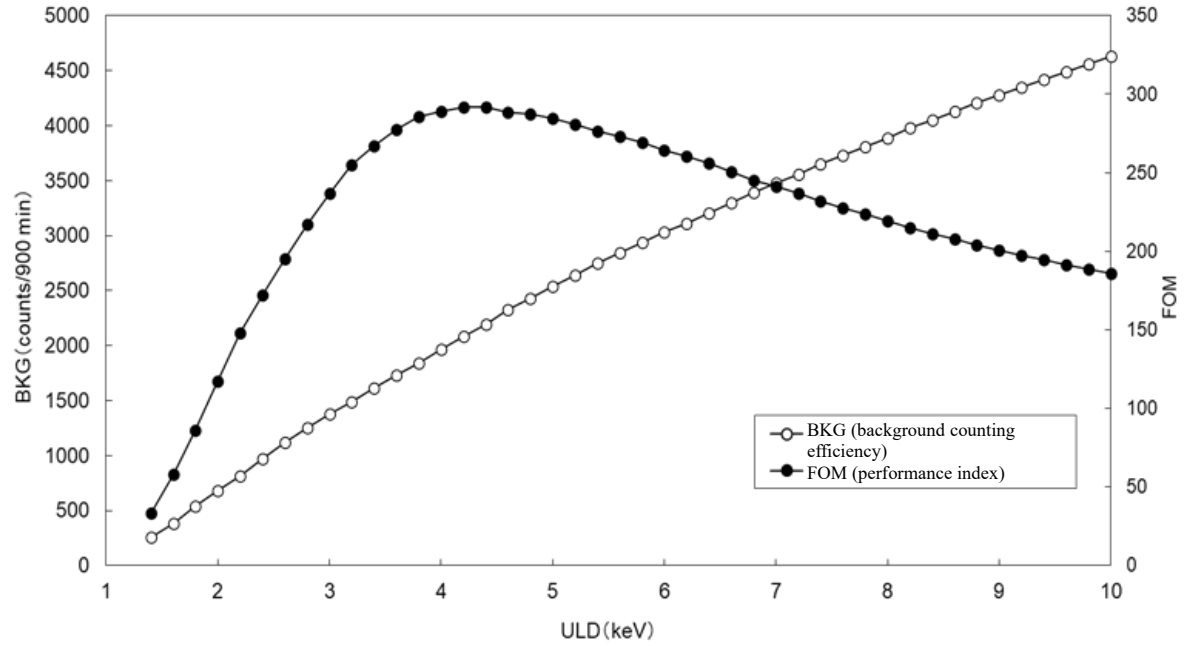


Figure 5.2 Setting of optimal window with FOM as an indicator

5.3.2 Setting the measurement conditions for determining the quenching index value using external standard sources

By irradiating a sample with a γ-ray source (^{137}Cs, ^{226}Ra, ^{133}Ba, etc.) of a certain intensity and using the pulse-height spectrum of Compton electrons generated by the interaction of emitted particles with the scintillator, the ratio of counts observed in different energy regions can be obtained as the quenching index value to understand the degree of quenching in the sample. Modern LSCs can monitor quenching index values before and after each tritium measurements, allowing accurate correction for temporal changes in the counting efficiency of the sample.

Because the energy distribution of Compton electrons is considerably higher than that of tritium β-rays, the measurement channel for obtaining the quenching index value of the former is set up separately from the tritium measurement channel. As with the setting of the tritium measurement conditions, it is possible to set the measurement conditions for obtaining the quenching index value, but it is acceptable to measure the quenching index value under the conditions set by the manufacturer at the time of delivery or maintenance inspection[92].

These instruments can alternate between tritium measurements and measurements to obtain quenching index values, allowing the sequential monitoring of the sample conditions (Figure 5.3).

[92] First, an external γ-ray source (^{137}Cs) is inserted near the sample, and the γ + β spectrum (the sum of the Compton electron spectrum from γ-ray and β-ray spectrum from tritium in the sample) is measured (usually for one minute). Then, the external γ-ray source is removed, and the β-ray spectrum (β-ray spectrum only from tritium) is measured (usually for one minute). Next, in each channel, the total value of only β-ray is subtracted from the total value of γ + β to obtain the Compton spectrum due to γ-ray only. The calculation method used for the quenching index value obtained using this Compton spectrum varies depending on the manufacturer and model; therefore, refer to the instruction manual of the employed measuring instrument for details.

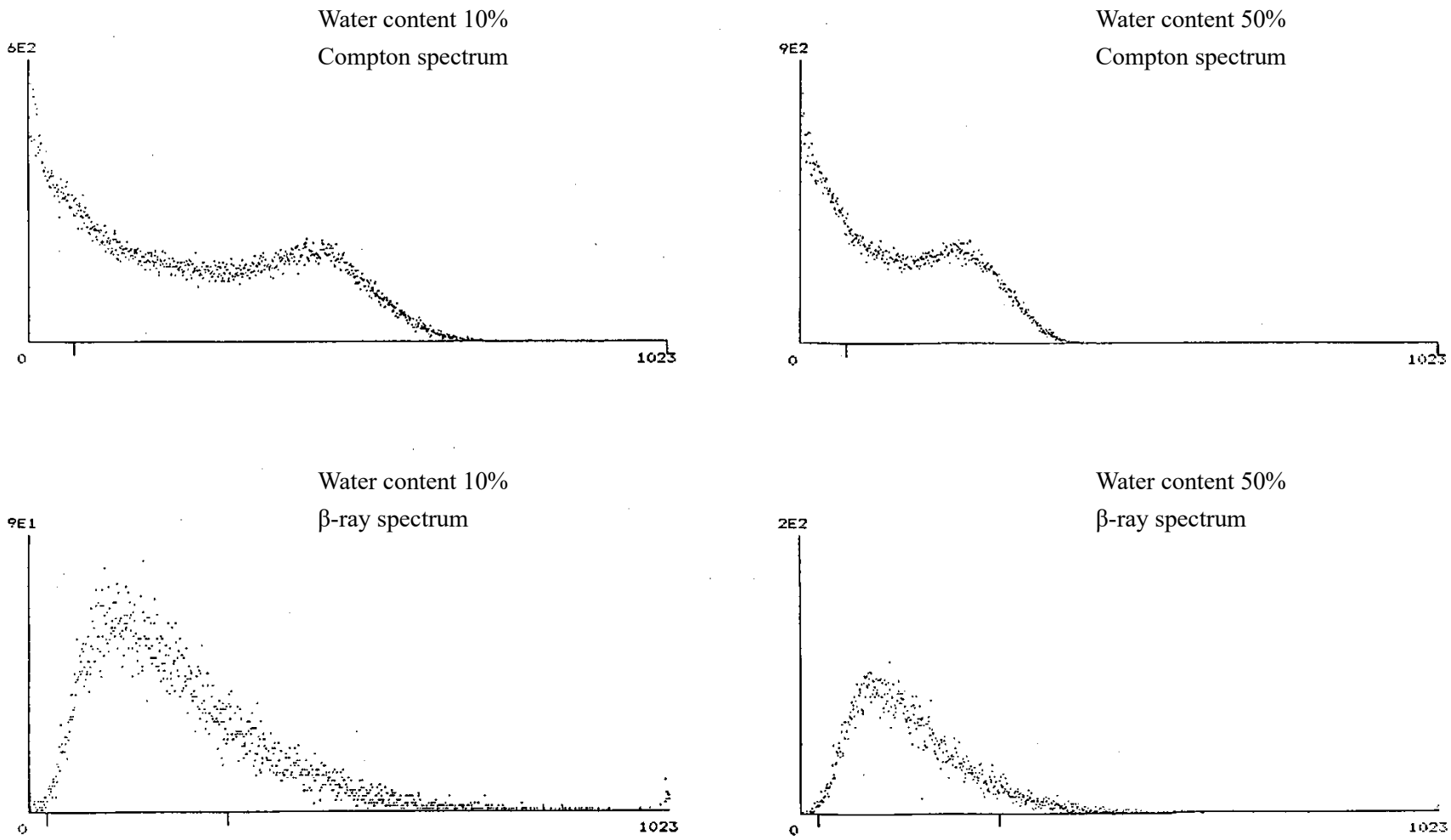


Figure 5.3 Example of spectral displacement due to quenching

5.4 Calibration: Preparation of quenching-correction curves

The quenching standard sample prepared using the method described in 5.1 Preparation of standard samples for quenching-correction curve is measured under the measurement conditions provided in 5.3 setting of measurement conditions to obtain a curve that correlates the counting efficiency of tritium with the quenching index value. The procedure for creating a quenching-correction curve is described below.

1) Arrange standard samples on the turntable in the order of decreasing or increasing water content.
2) Set the measurement channels for tritium (LLD and ULD) and that for the quenching index value (LLD) based on the measurement conditions described in 5.3.1 Setting the measurement conditions based on the figure of merit (FOM) and 5.3.2 Setting the measurement conditions for determining the quenching index value using external standard sources or to predetermined conditions.
3) For each standard sample, tritium concentration measurement is performed for ten to several tens of minutes, and counting efficiency $E(\%)$ is calculated by dividing the obtained counting rate (cpm) by the amount of tritium added (Bq).

   The quenching index value, which is measured prior to tritium measurement, is read out and recorded from the output result.
4) Plot all data on a linear graph, with counting efficiency E (%) being represented on the vertical axis and the quenching index value on the horizontal axis. Using the quenching index value as a variable, the quenching-correction curve is assumed to be a quadratic or cubic equation and displayed as a numerical expression using the least squares method (Figure 5.4).

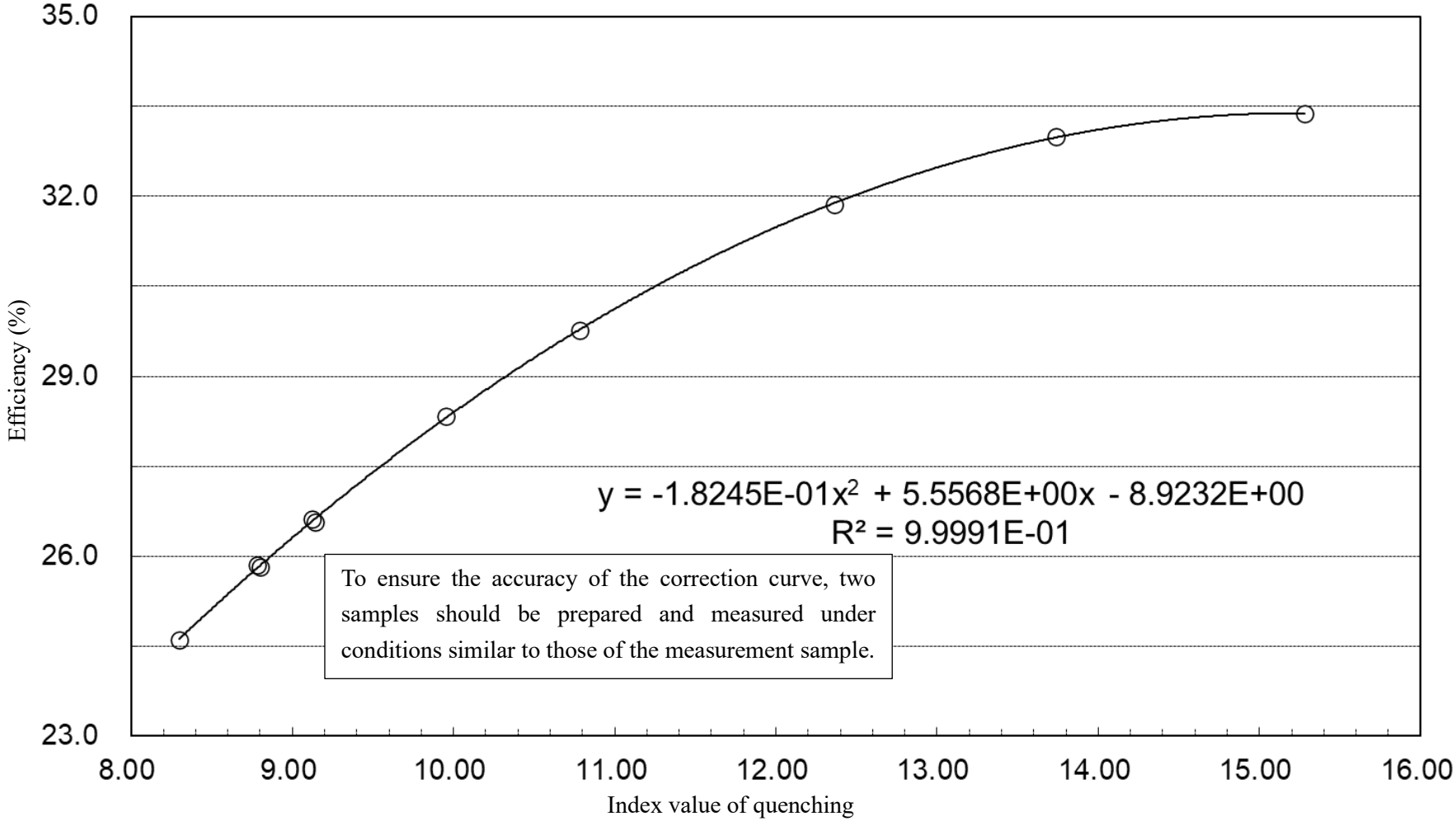


Figure 5.4 Example of a quenching-correction curve

Chapter 6 Measurement

The sample water obtained previously (refer to Chapters 2, 3 and 4) is mixed with an emulsified scintillator to prepare the measurement sample, and tritium is measured using a low-background LSC.

6.1 Preparation of measurement samples

The following laboratory equipment and reagents are required in this section

(1) Laboratory equipment
- A measurement container (use a container made of fluoroplastic (100 mL), low-potassium glass (20 mL), polyethylene (20 or 145 mL), etc.)
- Water bath (to be used as needed.)

(2) Reagents
- Emulsified scintillator (use a commercially available product. See [Explanation D])

(3) Procedure

1) The sample water volume is obtained by multiplying the optimum measurement liquid volume, which is determined from the LSC and measuring container used, by the optimum water retention rate of the emulsified scintillator[93].
2) For example, if an emulsified scintillator and 100-mL measuring container are used, the sample water volume should be 40–50 mL and emulsified scintillator volume should be 60–50 mL for a total measurement volume of 100 mL. When using a 20 mL measuring container, the volume of the sample water should be 8–10 mL and that of the emulsified scintillator should be 12–10 mL for a total volume of 20 mL.
3) Depending on the employed emulsified scintillator, using certain mixing ratios tends to separate the mixture into two phases; therefore, mixing in such ranges should be avoided[94].
4) Take a precise volume of the sample water (specific gravity of water is 1 g/cm^3), and transfer it to a measuring container.
5) Accurately add the emulsified scintillator to the sample water using an automatic burette, etc., and mix to obtain the optimum measurement liquid volume shown in Step 1.
6) Cover the measuring container, and shake it gently.
7) If the scintillator does not require heating, it can be mixed with samples uniformly by simply shaking the measuring container. For scintillators that require heating, use a water bath to heat the measuring container by immersing it in warm water (~50°C), and mix the mixture by shaking it until it becomes clear. If it is heated too much, it will emulsify and turn white but

[93] Because the optimum measurement liquid volume varies slightly depending on the LSC and measuring container used, it is necessary to consider the optimum measurement volume and optimum water retention rate of the emulsified scintillator in advance if high counting efficiency is desired.
The optimum measurement liquid volume is usually determined so that the value of (counting efficiency) x (measurement liquid volume) becomes maximum.
Similarly, the optimum water retention rate of the emulsified scintillator should be the maximum value of (counting efficiency) x (water retention rate).

[94] Refer to the instruction manual for the emulsified scintillator used.

will become transparent as it cools. Before use, check the instruction manual for the emulsified scintillator.

8) After washing the outside of the measuring container with distilled water, wipe-off water, handprints, etc. with paper towels, etc., and place the container in a cool, dark place to stabilize the sample. Note that if measurements are conducted immediately after mixing and shaking (Steps 5–7), abnormally high count values may be obtained or count variability may be large due to false counts caused by chemiluminescence. Figures 6.1–6.4 show the results of an experiment in which the background measurement sample and emulsified scintillator (Ultima Gold LLT and Ultima Gold uLLT were used) were mixed in a fluoroplastic vial (using an antistatic spray), and measurements were repeated for 60 min each time for one week (168 times). High counting rates were observed in the first to the fourth measurements (4 h). The primary reasons for this observation are likely the effects of chemiluminescence and static electricity, which decayed quickly, and a stable count rate was obtained after approximately 5 h (Figures 6.1 and 6.2). Furthermore, counting rates gradually decreased over the following week (Figures 6.3 and 6.4). A more stable counting rate can be obtained if the sample is left in the instrument or in an incubator at approximately 15°C for 24 h to approximately one week after preparation. If a quick measurement is required, a settling time of approximately 5 h may be effective. However, these results are only examples, and the time required for the stabilization of the counting rate may vary depending on the scintillator, container, and storage environment. Therefore, confirming the appropriateness of the settling time is necessary by conducting a similar study at each laboratory, considering the desired detection level.

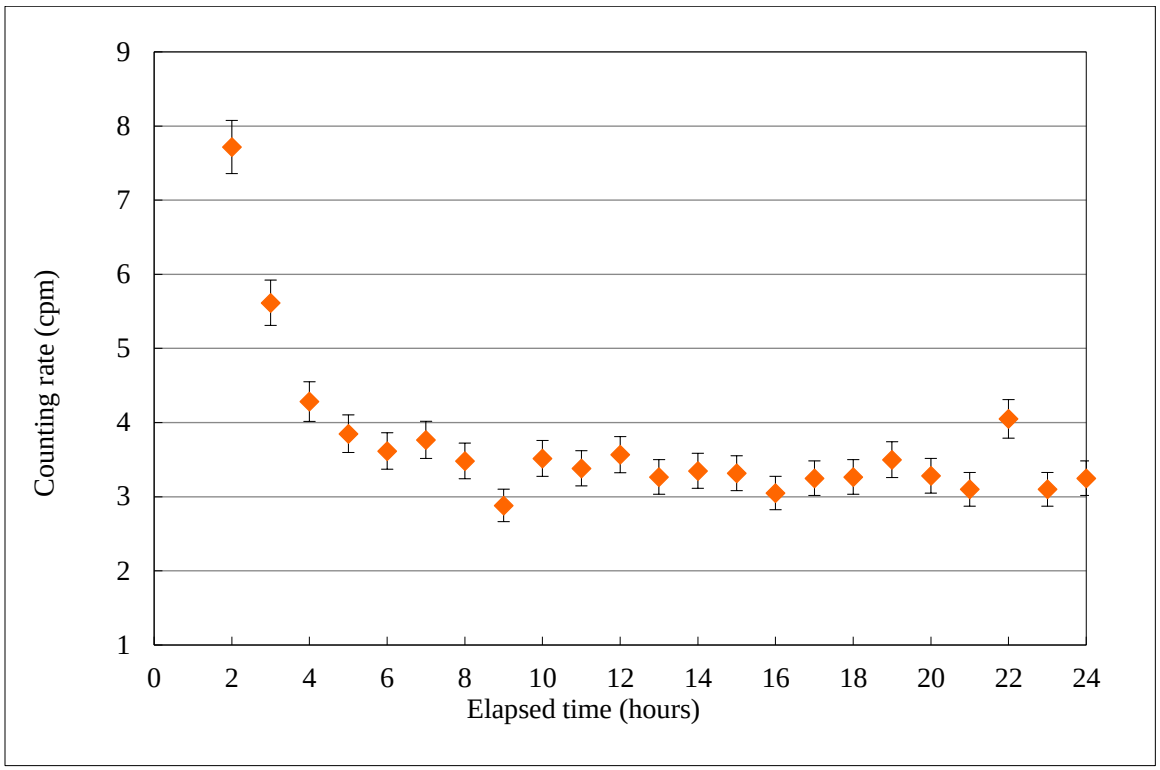


Figure 6.1 Temporal changes in the counting rate immediately after mixing Ultima Gold LLT (2*–24 h)

* The first measurement (first 60 min) showed a high value of 170.983 cpm; therefore, the vertical axis was expanded after the second measurement.

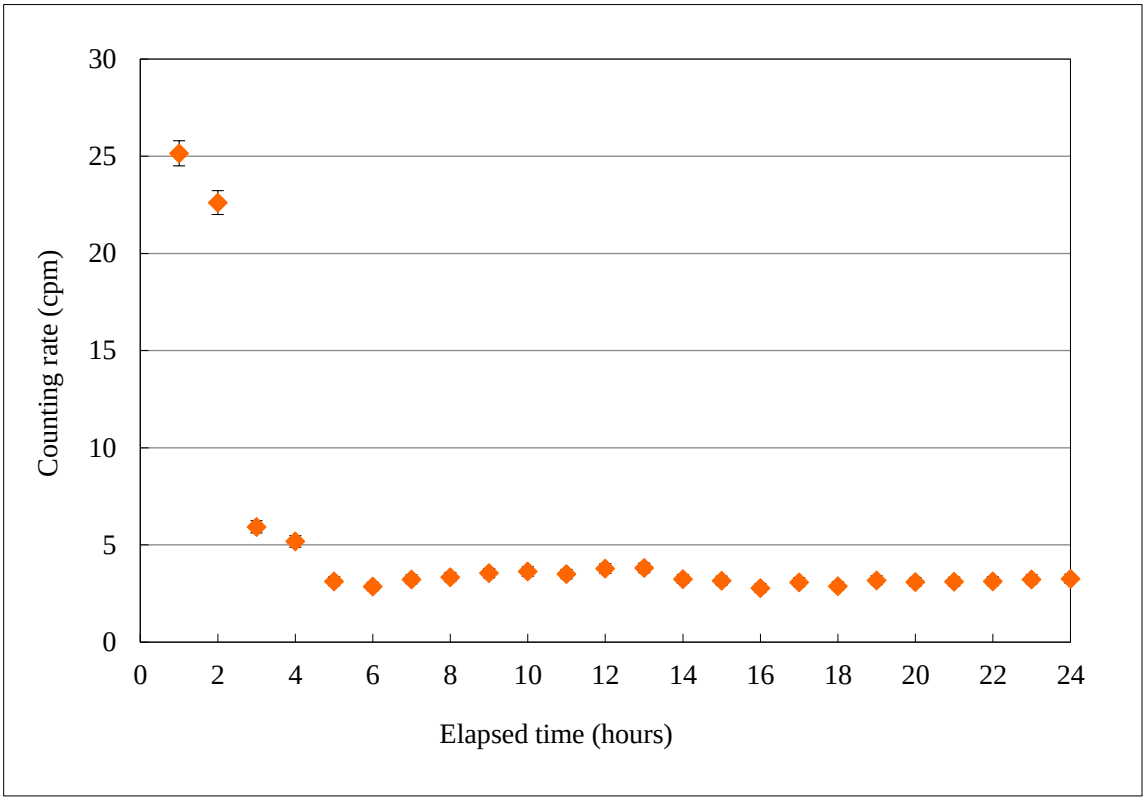


Figure 6.2 Temporal changes in counting rate immediately after mixing Ultima Gold uLLT (1–24 h)

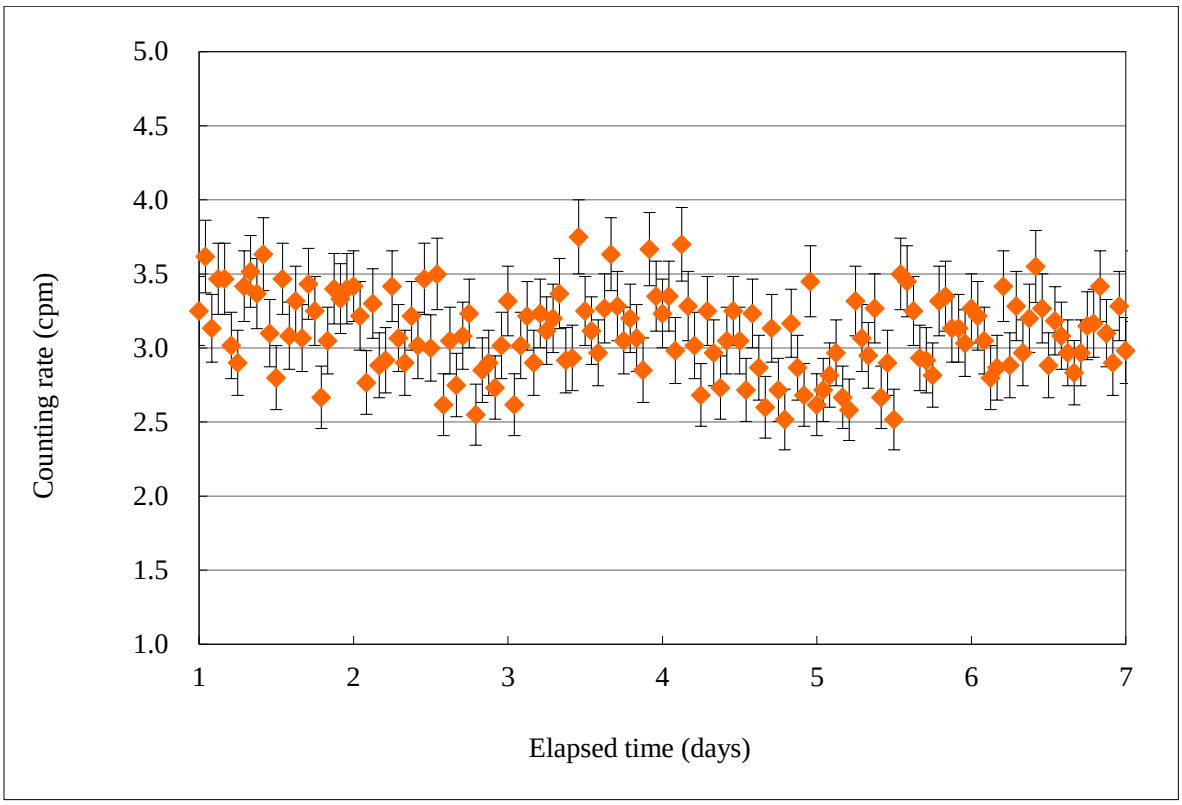


Figure 6.3 Temporal changes in counting rate immediately after mixing Ultima Gold LLT (1–7 days)

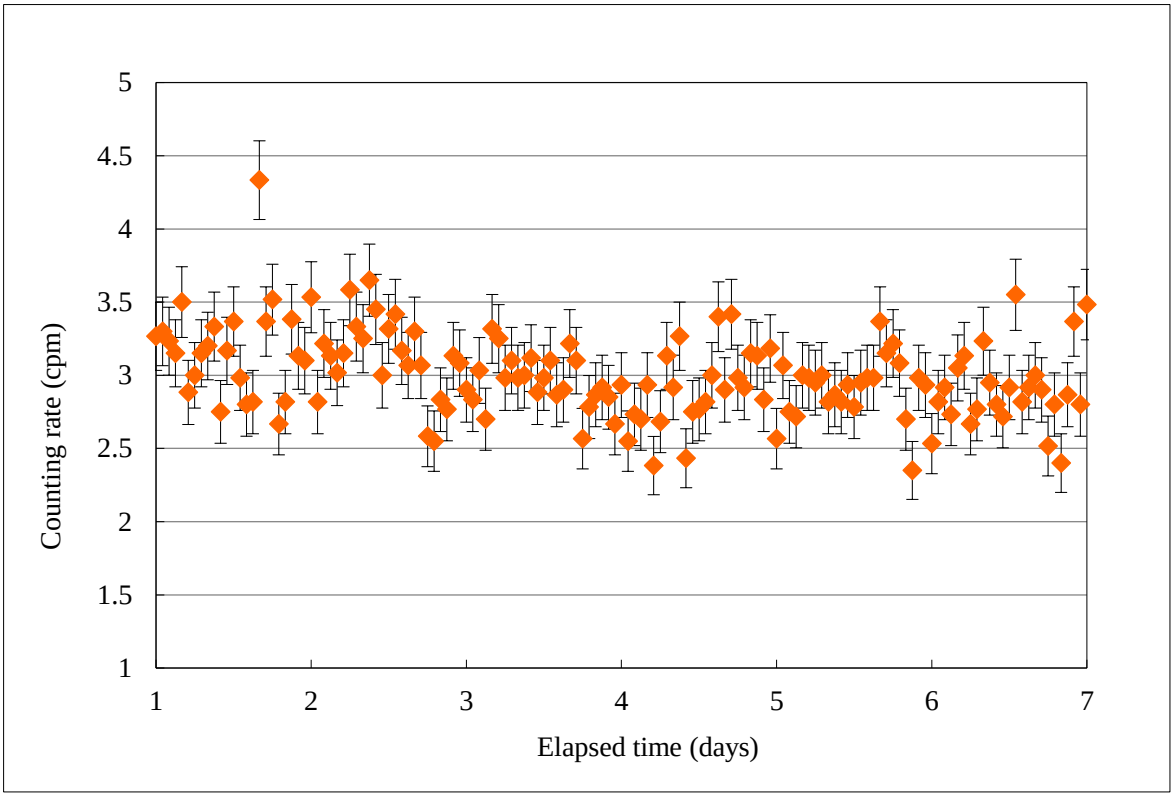


Figure 6.4 Temporal changes in counting rate immediately after mixing Ultima Gold uLLT (1–7 days)

6.2 Measurement

6.2.1 Sample measurement

1) Set the measurement conditions of the LSC to the optimum conditions for tritium measurement according to 5.3 Setting of measurement conditions.
2) Place the unknown and background samples[95] that have been left for approximately one day to one week after sample preparation on the turntable. Further, subject each sample to antistatic spraying. To detect abnormalities arising from fluctuations in background measurements in the measuring instrument or environmental conditions during the measurement period, it is recommended to arrange multiple background samples at regular intervals between unknown samples.
3) For each sample, repeat 10 to 50 min measurements so that the total measurement time will be 100–1,000 min.

   Repeated measurements are preferable than a single measurement over a long period of time, and abnormal values should be rejected according to 6.2.3 Data rejection test.

   The total measurement time and number of repetitions for background samples should be the same as those for unknown samples.

6.2.2 Precautions for measurement

Pay attention to the following points to perform accurate measurements.

(1) Selection of the measuring container

Measuring containers are made of glass (low-potassium glass), fluoroplastic, polyethylene, etc. Low-potassium glass vials have higher counting efficiency and exhibit lesser variation due to individual differences than fluoroplastic vials; however, they have a higher background counting rate. Because fluoroplastic vials are not produced specifically for liquid scintillation counting, commercially available general-purpose products are used. However, because any variation in the vial's wall thickness will affect counting efficiency, products with no variation in the thickness should be selected by, for example, setting tolerance standards for the weight range of the vial. Polyethylene vials have a lower background counting rate and somewhat higher counting efficiency than low-potassium glass vials but are not suitable for long-duration measurements because organic solvents tend to permeate the vial walls.

(2) Stability of measured samples

Emulsified scintillators are typically used in a mixture with an aqueous solution. In the case of tritium concentration measurement, although as much water as possible is mixed with the emulsified scintillator to increase the FOM value, to maintain the gel state, a water content of approximately 40%–50% is usually used.

Note that depending on the water content, samples may easily separate into two phases; therefore, avoid using samples at such water content values.

Note that the background counting rate or counting efficiency may vary depending on the manufacturing lot of an emulsified scintillator.

[95] Background samples are measured at the beginning and end of a measurement batch.

(3) Measurement room environment

The background counting rate may be high, especially in the tritium measurement area, due to air emission from the α-rays of radon and its descendants present near the detector.

In addition, false counting due to static electricity may be observed when fluoroplastic vials are used during dry periods, such as winter.

To reduce these effects, attention shall be paid to the selection of building materials, ventilation, humidity, and other controls.

(4) Chemiluminescence

If a sample is measured immediately after preparation, the count may increase. This is caused by chemiluminescence, whose pulse wave height is very small and overlaps with the tritium spectrum.

As a preventive measure, as most chemiluminescence decreases exponentially with time, it is recommended to leave samples in the measuring instrument or in a thermostatic chamber such as an incubator at approximately 15°C for approximately 24 h to 1 week after sample preparation before starting measurement. (See 6.1 Preparation of measurement samples for more details.)

(5) Static electricity

LSCs are usually installed in air-conditioned rooms, and false counting due to static electricity may occur, especially when fluoroplastic vials are used. This is because fluoroplastic as a material is easily charged and may become charged when moving on a turntable.

As a preventive measure, spraying an antistatic spray[96] onto measurement vials before starting measurement and using the static electricity removal mechanism (ion shower) built into the LSC are effective.

The method of unconditionally rejecting the first few data of repeated measurements is also useful as this effect is likely to reflect in the data immediately after replacing the measurement sample.

6.2.3 Data rejection test

Typical methods and examples of rejection tests are shown in Explanation E. Statistical processing is performed to remove outliers from counts obtained by repeated multiple measurements, and rejection tests are performed on the data.

[96] A semiconductor-coating-type spray is preferred as the antistatic spray. Spray thoroughly so that the vial surface is evenly wetted, and the coating continues to the bottom of the vial.

6.2.4 Calculation of radioactivity concentration

The radioactivity concentration is calculated by subtracting the background counting rate from the sample counting rate, and then using counting efficiency obtained from the quenching-correction curve, measurement sample volume, and half life correction factor.

The remaining data after rejecting outliers are used in calculations according to 6.2.3 Data rejection test.

In the formula below, " $\pm$ " represents standard uncertainty ($k = 1$).

(1) Sample counting rate (including background)

Divide the total count by the measurement time to obtain the counting rate (including background) of the sample.

$$\text{Sample counting rate (including background) (cpm)} = \frac{N_s \pm \sqrt{N_s}}{t_s}$$

where N_s: the total count including background

t_s : the sample measurement time (min)

(2) Background counting rate

Divide the total count as well as sample count by the measurement time to obtain the counting rate of the background sample.

$$\text{Background counting rate (cpm)} = \frac{N_b \pm \sqrt{N_b}}{t_b}$$

where, N_b: total count of background sample

t_b : measurement time for background sample (min)

(3) Net counting rate

Subtract the background counting rate from the sample counting rate to obtain the net counting rate.

$$\text{Net counting rate (cpm)} = \left(\frac{N_s}{t_s} - \frac{N_b}{t_b}\right) \pm \sqrt{\frac{N_s}{t_s^2} + \frac{N_b}{t_b^2}}$$

(4) Counting efficiency

Determine the average quenching index value measured alternately with tritium measurements for samples.

nWhen using the data of n measurements, the quenching index value is

$$R_{av} = \frac{R_1 + R_2 + \cdots + R_n}{n}$$

Substitute this value into the numerical expression (quadratic or cubic) of the quenching-correction curve created according to 5.4 Calibration: Preparing quenching-correction curve to obtain counting efficiency (%) for samples.

(5) Calculation of radioactivity concentration

1) In water samples,
the tritium concentration is determined according to the following equation:

$$A = \left[\left(\frac{N_s}{t_s} - \frac{N_b}{t_b}\right) \pm \sqrt{\frac{N_s}{t_s^2} + \frac{N_b}{t_b^2}}\right] \times \frac{100}{Eff} \times \frac{1}{60} \times \frac{1000}{V} \times \frac{1}{R} \times \frac{1}{F}$$

where

A : Radioactivity concentration of tritium at the time of sample collection (Bq/L)

Eff : Counting efficiency (%)

V : Sample volume (mL)

R : In the case of distillation, it is 1. In the case of the electrolytic concentration, it is the concentration factor.

F : Half life correction factor $= \left(\frac{1}{2}\right)^{\left(\frac{t}{12.32}\right)}$

Where t: time elapsed from the sample collection date to the date of measurement (converted to years)

12.32 : Half life of tritium (years)

.

2) For biological samples (TFWT),
the tritium concentration is determined according to the following equation:

$$B_1 = \left[\left(\frac{N_s}{t_s} - \frac{N_b}{t_b}\right) \pm \sqrt{\frac{N_s}{t_s^2} + \frac{N_b}{t_b^2}}\right] \times \frac{100}{Eff} \times \frac{1}{60} \times \frac{1000}{V} \times \frac{1}{R} \times \frac{1}{F}$$

$$B_{TFWT} = B_1 \times \left(1 - \frac{Z}{100}\right)$$

where

B_1 : Radioactivity concentration of TFWT (Bq/L)

Eff : Counting efficiency (%)

V : Sample volume (mL)

R : In the case of distillation, it is 1. In the case of the electrolytic concentration, it is the concentration factor.

B_{TFWT} : Radioactivity concentration of TFWT in raw samples (Bq/kg of raw mass)

Z : Dry residual fraction (%)[97]

F : Half life correction factor $= \left(\frac{1}{2}\right)^{\left(\frac{t}{12.32}\right)}$

Where t: Time elapsed from the sample collection date to the date of measurement (converted to years)

12.32 : Half life of tritium (years)

3) For biological samples (OBT),
the tritium concentration is determined according to the following equation:

[97] Note that the dry residual fraction is a dimensionless quantity, but the units are converted from Bq/L to Bq/kg of raw mass.

$$B_2 = \left[\left(\frac{N_s}{t_s} - \frac{N_b}{t_b}\right) \pm \sqrt{\frac{N_s}{t_s^2} + \frac{N_b}{t_b^2}}\right] \times \frac{100}{Eff} \times \frac{1}{60} \times \frac{1000}{V} \times \frac{1}{F}$$

$$B_{OBT} = B_2 \times \left(\frac{X}{Y} \times \frac{Z}{100}\right)$$

where

B_2 : Radioactivity concentration of OBT (Bq/L)

Eff : Counting efficiency (%)

V : Sample volume (mL)

B_{OBT} : Radioactivity concentration of OBT in raw samples (Bq/kg of raw mass)

Z : Dry residual fraction (%)

X : Combustion-generated water (g)

Y : Burned sample weight (g)

F : Half life correction factor $= \left(\frac{1}{2}\right)^{\left(\frac{t}{12.32}\right)}$

Where t: Time elapsed from the sample collection date to the date of measurement (converted to years)

12.32 : Half life of tritium (years)

Because the above formula is based on the assumption that there is no loss in the recovery of combustion-generated water, it is recommended to determine the hydrogen content in the combustion sample using an elemental analyzer and calculate the radioactivity concentration of OBT (Bq/kg of raw mass) using the following formula.

$$B_{OBT}\ \text{(Bq/kg of raw mass)} = B_2\ \text{(Bq/L)} \times \frac{\text{Hydrogen content (\%)}}{100} \times \frac{18}{2} \times \left(\frac{Z}{100}\right)$$

4) For atmospheric samples (HTO),

in the method that uses molecular sieves and method that utilizes silica gel, the tritium concentration is determined according to the following equation.

$$C_1 = \left[\left(\frac{N_s}{t_s} - \frac{N_b}{t_b}\right) \pm \sqrt{\frac{N_s}{t_s^2} + \frac{N_b}{t_b^2}}\right] \times \frac{100}{Eff} \times \frac{1}{60} \times \frac{1000}{V} \times \frac{1}{F}$$

$$C_{HTO} = \frac{C_1 \times M}{Q \times 1000}$$

where

C_1 : Radioactivity concentration of HTO water (Bq/L)

Eff : Counting efficiency (%)

V : Sample volume (mL)

C_{HTO} : Atmospheric HTO concentration (Bq/m^3 in air)

M : Water volume collected from atmospheric moisture (g)

Q : Sampling flow rate (m^3)

F : Half life correction factor $= \left(\frac{1}{2}\right)^{\left(\frac{t}{12.32}\right)}$

Where t: Time elapsed from the sample collection date to the date of measurement (converted to years)

12.32 : Half life of tritium (years)

In the method that uses a dehumidifier and the passive method, the tritium concentration of atmospheric water in a sample (Bq/L) is obtained according to 1) In water samples. However, when calculating the tritium concentration in air (Bq/m3), it is calculated according to the following formula.

$$C_{HTO} = C_1 \times d_v \times \frac{1}{1000}$$

C_1 : Radioactivity concentration of HTO water (Bq/L)
C_{HTO} : Atmospheric HTO concentration (Bq/m^3 in air)
d_v : Absolute humidity (g/m^3)

5) In atmospheric samples (HT),
the tritium concentration is determined according to the following equation:

$$C_2 = \left[\left(\frac{N_s}{t_s} - \frac{N_b}{t_b}\right) \pm \sqrt{\frac{N_s}{t_s^2} + \frac{N_b}{t_b^2}}\right] \times \frac{100}{Eff} \times \frac{1}{60} \times \frac{1000}{V} \times \frac{1}{F}$$

$$C_{HT} = \frac{C_2 \times (P + N)}{Q \times 1000} \times \frac{100}{L}$$

where

C_2 : Tritium water produced by the oxidation of HT
radioactivity concentration (Bq/L)
Eff : Counting efficiency (%)
V : Sample volume (mL)
C_{HT} : Atmospheric HT concentration (Bq/m^3 in air)
P : Weight increase in the palladium column (g)
N : Amount of water recovered from oxidation (weight increase in the HT column) (g)
Q : Sampling flow rate (m^3)
L : Palladium-catalyzed oxidation efficiency (%)
F : Half life correction factor $= \left(\frac{1}{2}\right)^{\left(\frac{t}{12.32}\right)}$

Where t: Time elapsed from the sample collection date to the date of measurement (converted to years)

12.32 : Half life of tritium (years)

.

6.2.5 Uncertainty

Uncertainty in measurements is used as an indicator of the reliability of a measurement result. It is defined as follows. Measurement uncertainty is a parameter[98] associated with a measurement result that characterizes the variation in a value, which can reasonably be attributed to the quantity being measured. It is important to note that measurement uncertainty is a value that represents the potential variability of a set of measurements, not the variability of each measurement result.

In conventional tritium analysis, it is a common practice to determine and report only the statistical uncertainty (counting error) of counts in radioactivity measurements. Although counting uncertainty is dominant in the analysis of low-tritium-concentration environmental samples, uncertainty factors exist in the entire tritium analysis process, including pretreatment and measuring instrument calibration. Therefore, it is necessary to evaluate uncertainty at each step. By evaluating uncertainty, it is possible to determine whether the tritium analysis results of each laboratory agree or disagree in proficiency tests and inter-laboratory comparisons. Furthermore, it is possible to improve the quality of analysis results by identifying the process that exhibits the highest uncertainty and taking steps to reduce it.

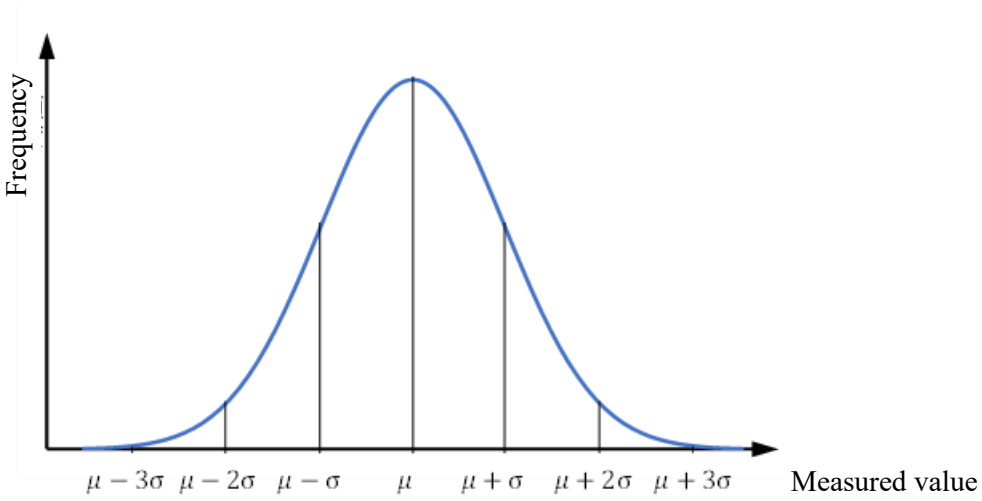
Refer to Explanation G for details regarding the method used for uncertainty evaluation in tritium analysis.

6.2.6 Lower detection limit

The lower detection limit in radioactivity measurements varies depending on the analysis sample, measurement time, background counting rate, etc., and it shall be set according to the purpose of analysis and measurement. Radioactivity detected or not is generally determined by whether or not the counting rate exceeds three times the statistical uncertainty of the net counting rate. Calculating the lower DL provides an indication of the radioactivity level at which a measurement is possible. Because environmental radioactivity is often weak and undetectable, it is advisable to obtain the lower DL when measuring analytical samples. It should be noted here that if radioactivity exceeds the lower DL, it most likely be detected; additionally, even if it is less than the limit, it may not necessarily be undetectable and can still be detected.

The calculation method used for the lower DL includes the Kaiser method described in the 2002 revision of this manual and the evaluation method according to the international standard ISO 11929. In the concept of each lower DL, the distribution of measured values must be considered. When a measurement target is repeatedly analyzed a sufficient number of times, the measured values are expressed in a mathematical model called a normal distribution or Gaussian distribution, with the mean at the top, as shown in Figure 6.5.

[98] JIS Z 8404-1: Measurement Uncertainty - Part 1, JIS Z 8404-1:2018 (2018)



μ: Average of measured values

σ: Standard deviation of the distribution of measured values

Figure 6.5 Distribution of measured values

Approximately 68% of measurements are in the $\mu \pm \sigma$ range, approximately 95% are in the $\mu \pm 2\sigma$ range, and approximately 99.7% are in the $\mu \pm 3\sigma$ range.

Several methods are available for evaluating the DL, but the method to be used depends on the requirements of the survey for which the measurement is conducted. When reporting the lower DL, the evaluation method employed and risk rate should be clearly stated.

Calculation methods used for the lower DL include the Cooper's method[99], Kaiser method[100,101], Currie's method[102], and evaluation method according to ISO 11929[103]. In this manual, evaluation using the Kaiser's method and ISO 11929 are described, and specific calculation examples are given in Explanation H.

[99] J. A. Cooper, Factors Determining the Ultimate Detection Sensitivity of Ge (Li) Gamma-Ray Spectrometers. *Nucl. Instrum. Methods*, **82**: 273-277 (1970).

[100] H. Kaiser, *Zum Problem der Nachweisgrenze* [On the Problem of the Detection Limit]. *Analytisehe Chemie*, **209**, 1-18 (1965).

[101] IUPAC Analytical Chemistry Division Commission on Spectrochemical and Other Optical Procedures for Analysis. Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis - III. Analytical Flame Spectroscopy and Associated Non-Flame Procedures, *Pure & Appl. Chem.*, **45**, 105-123 (1976).

[102] L. A. Currie, Limits for Qualitative Detection and Quantitative Determination Application to Radiochemistry. *Anal. Chem.*, **40**,586-593 (1968).

[103] International Organization for Standardization. ISO 11929-4:2022. Determination of the Characteristic Limits (Decision Threshold, Detection Limit and Limits of the Coverage Interval) for Measurements of Ionizing Radiation — Fundamentals and Application — Part 4: Guidelines to applications. (2022)

Chapter 7 Quality Assurance

In addition to conducting analyses and measurements in accordance with the procedures described in this method, it is extremely important to ensure traceability to national standards, etc. and to conduct daily inspections to ensure the integrity of the equipment. Continuous implementation of these practices will demonstrate to third parties that the quality of analytical results is assured. To guarantee the quality of analysis results, it is desirable to follow the concept of ISO/IEC 17025, which can be broadly classified into internal quality control conducted by analyzers/measurers and external quality control in which they participate in proficiency tests conducted by external organizations.

7.1 Internal quality control

7.1.1 Ensuring traceability

In tritium analysis results, radioactivity (Bq) and weight (kg) are parameters for which traceability shall be ensured. The traceability of the former is required for LSCs calibrated using a standard solution source, and the traceability of the latter should be ensured for electronic balances used in the preparation of measurement samples. When users prepare efficient radiation sources, they can obtain standard solution sources traceable to national standards, with calibration certificates issued by calibration laboratories under the calibration laboratories registration system based on the Measurement Act. For electronic balances, calibration services are provided by the respective manufacturers, and maintenance and inspection, including the issuance of calibration certificates, should be performed. Equipment calibration should be conducted at an appropriate frequency, and the expiration date of calibration should be set and controlled. During the period of validity, daily inspections, as described in 7.1.2, should be performed to verify that no changes have occurred in equipment that may affect analytical results.

Traceability should be ensured for records and other documents that accompany analytical results. Specifically, it is important that collection record sheets, which record the date and place of sample collection, unique numbers (analysis numbers, etc.) that identify analyzed samples, and various records and forms generated during analyses and measurement operations, are managed in a seamlessly linked manner.

7.1.2 Daily inspection

Inspection items and methods for equipment used in tritium analyses and measurements are described below. To confirm that equipment is sound and can be used, it is necessary to establish acceptance criteria for each inspection item. It is recommended to establish provisional criteria with the initial data obtained experimentally, and once data are accumulated, the acceptance criteria should be re-established[104] through statistical processing. Because it is sufficient to confirm that no changes affecting analysis results have occurred in the instrument, a different method may be used to confirm this. The daily inspection date, person in charge, and inspection results should be recorded.

[104] It is easy to determine the mean and standard deviation and use a range of $\pm k\sigma$ (2 or 3 as k) centered on the mean as the acceptance criterion. In addition, if equipment maintenance is performed or if emulsified scintillators are changed, confirm whether the acceptance criteria should be revised.

If the daily inspection results do not meet the acceptance criteria, the use of the equipment should be suspended, and the cause of the problem should be investigated and resolved. If the cause is not eliminated via re-measurement by users or equipment re-setting, inspection and repair by the respective manufacturers should be performed.

(1) Liquid scintillation counter

Periodically inspect the LSC to ensure that no changes have occurred in the instrument that will affect analytical results. In terms of frequency, it is recommended to conduct this test every time a measurement is performed.

・ Counting efficiency

If a standard source[105] containing a certain amount of radioactivity is measured under the same conditions and the obtained count values (or count rates) are within acceptable standards, it can be confirmed that counting efficiency has not changed enough to affect results. When checking changes in counting efficiency, it is necessary to consider the decay of radioactive nuclides contained in the standard source.

・ Cooling performance

LSCs equipped with coolers maintain a constant temperature inside the measuring instrument. By maintaining a low temperature in the measuring instrument, it is possible to reduce incidental coincidence counts caused by dark current (dark noise) generated in the photomultiplier tube (PMT) and to suppress changes in quenching caused by temperature changes in the measurement sample. The set temperature should be approximately 15°C (refer to the equipment's operation manual for the set temperature), and it should be controlled within a fluctuation range of ±3°C.

The use of a thermometer with a sensor is convenient for controlling the temperature inside the measuring device. Checking the temperature without opening and closing the measurement device can suppress temperature changes inside the device and reduce the influence of photoluminescence caused by fluorescent molecules and visible light.

・ Installation environment

Ensure that the LSC is installed in a location that has appropriate climate control and that the installation environment is maintained. The room temperature should be approximately 23°C–25 °C, with a variation range of ±2°C or less, and relative humidity should be kept at 30 %–80 %. Although it does not directly affect the quality of analysis results, it is essential that the load-bearing capacity of the floor be sufficient for the weight of the equipment when installing LSCs with a large total weight due to lead shielding.

(2) Electronic balance

Inspect the electronic balance periodically to ensure that no changes have occurred in the instrument that will affect analysis results. It is desirable to conduct pre-use inspections before each use and periodic inspections on a monthly or other basis.

・ Pre-use inspection

[105] It does not have to be the same shape as the actual measuring container used. Tritium-sealed sources, such as those supplied with the equipment at the time of delivery, can be used. When using an unsealed source, such as a source for preparing quenching-correction curves, the absence of alteration over a long period of time should be confirmed by no change in the mass or quenching indices.

This is an inspection to be performed before using the balance. Balances with built-in weights should be calibrated internally in advance. Conduct a pre-use inspection of the electronic balance using a weight[106] that is close to the weight of the sample to be weighed (or at the lower limit of the usable range), and confirm that the weighing result is within the permissible standard.[107] It is even better if the same inspection is performed after using the electronic balance.

- Periodic inspection

  Check the sensitivity of the electronic balance using a weight that is close to the maximum weighing value of the electronic balance to be used. Balances with built-in weights should be calibrated internally in advance. The grade and acceptance criteria of weights used may conform to those employed in pre-use inspection. This inspection should be performed at regular intervals, and it is recommended to perform it approximately once a month.

7.2 External quality control

7.2.1 Interlaboratory comparison

The validity of the measurement and analysis process can be confirmed by conducting an inter-comparison analysis with another laboratory (preferably an ISO/IEC17025-accredited laboratory) using the same sample, confirming that there is no significant difference between the results of the two analyses.

7.2.2 Proficiency test

Participating in a proficiency test conducted by an external organization (preferably one with ISO/IEC 17043 accreditation) and comparing the analysis results of the tested product with the added value (assigned value) can objectively demonstrate the proficiency of the testing laboratory. In the case of the proficiency test based on ISO/IEC 17043, performance evaluation methods for participating laboratories include z-scores and En numbers.

[106] Weights with calibration certificate (OIML (JIS) standard F2 or higher) are recommended.

[107] Although the tolerance criteria must be determined based on weighing uncertainty, minimum weighing value, and safety factor, an initial control range of 0.5% may be set (e.g., for a 10-g weight, the tolerance criteria will be 9.95–10.05 g).

Explanation

Explanation A Electrolytic Enrichment of Tritium

A.1 Results of study on the electrolytic enrichment method using metal electrodes

In addition to the Fe–Ni electrode combination, electrolytic enrichment with metal electrodes can be performed with Ni–Ni electrodes. A comparison of the two methods was performed. Observation of the electrode surface during and after electrolytic enrichment revealed no particular abnormality, and no discoloration, elution, or other changes were observed on the electrode surface.

An alkaline solution was electrolytically concentrated from an initial water volume of 500 mL to a final water volume of approximately 50 mL according to this analytical method. The results for the Fe–Ni and Ni–Ni electrodes are shown in Tables A.1 and A.2, respectively. Analysis was performed by alternating the two types of electrodes, as shown in Figure A.1.

A higher tritium residual ratio$R$ (approximately 0.82–0.86) was obtained for the Fe–Ni electrode than the Ni–Ni electrode. However, Fe–Ni electrodes must be stored carefully, for example, in sodium hydroxide solution, because Fe tends to rust when not in use. The electrode type should be selected appropriately for the situation.

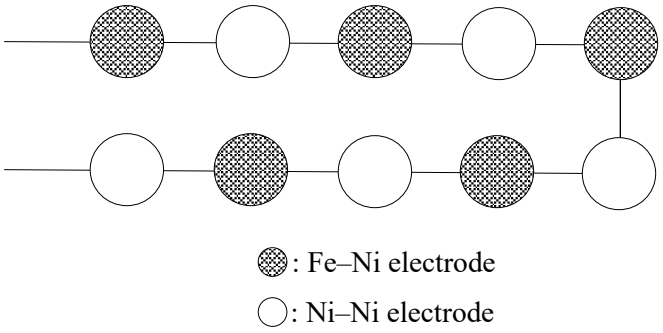


Figure A.1 Electrode layout

The relationship between the tritium concentration and water volume in water electrolysis is defined as follows:

$$Vf/Vi = ((Tf \times Vf)/(Ti \times Vi))^{\beta a}$$

where

Vi : Water volume before enrichment
Vf : Water volume after enrichment
Ti : Tritium concentration before enrichment
Tf : Tritium concentration after enrichment
$\beta\alpha$: Apparent tritium separation factor
As the value of $\beta\alpha$ increases, the tritium loss during electrolysis decreases exponentially.

In addition, each parameter involved in enrichment (N, Z, and R) is defined as follows:

$N = Vi/Vf$: Volume enrichment ratio
$Z = Tf/Ti$: Tritium enrichment rate (device constant)
$R = (Tf \times Vf)/(Ti \times Vi)$: Tritium residual rate (tritium recovery rate)

$$\beta\alpha = \frac{\log(Vf/Vi)}{\log((Tf \times Vf)/(Ti \times Vi))}$$

For actual calculation, R and N are used to obtain the pre-enrichment tritium concentrationTi from the following formula.

$$Ti = (Tf)/(N \times R)$$

R is obtained from the measurement results of a tritium standard sample electrolyzed under the same conditions.

Table A.1 Electrolytic enrichment results for Fe–Ni electrodes

Procedure No.	Sample No.	*Vi* (g)	*Vf* (g)	*N*	*Ti* (Bq/L)	*Tf* (Bq/L)	*Z*	*R*	*βa*
1	Fe–Ni-1	497.5	45.97	10.82	0.0640	0.570	8.91	0.8230	12.22
	Fe–Ni-2	497.5	48.51	10.26	0.0635	0.548	8.64	0.8422	13.55
	Fe–Ni-3	497.5	48.75	10.20	0.0637	0.543	8.54	0.8372	13.07
	Average		47.74	10.43	0.0637	0.554	8.70	0.8341	12.95
	Standard deviation		1.54	0.34		0.87	0.19	0.010	0.67
	Coefficient of variation (%)		3.23	3.28		2.61	2.20	1.19	5.20
2	Fe–Ni-4	497.5	53.47	9.30	0.0367	0.284	7.75	0.8326	12.17
	Fe–Ni-5	497.5	48.84	10.19	0.0378	0.321	8.48	0.8321	12.63
	Fe–Ni-6	497.5	48.78	10.20	0.0377	0.322	8.54	0.8370	13.05
	Fe–Ni-7	497.5	49.17	10.12	0.0377	0.326	8.66	0.8561	14.90
	Fe–Ni-8	497.5	48.68	10.22	0.0368	0.311	8.44	0.8261	12.17
	Average		49.79	10.01	0.0373	0.313	8.37	0.8368	12.98
	Standard deviation		2.07	0.40		1.03	0.36	0.012	1.13
	Coefficient of variation (%)		4.15	3.96		5.49	4.28	1.37	8.72

Table A.2 Electrolytic enrichment results for Ni–Ni electrodes

Procedure No.	Sample No.	*Vi* (g)	*Vf* (g)	*N*	*Ti* (Bq/L)	*Tf* (Bq/L)	*Z*	*R*	*βa*
1	Ni–Ni-1	497.5	51.47	9.67	0.0637	0.418	6.57	0.6801	5.89
	Ni–Ni-2	497.5	51.68	9.63	0.0633	0.424	6.69	0.6947	6.22
	Ni–Ni-3	497.5	52.00	9.57	0.0632	0.415	6.58	0.6873	6.02
	Average		51.72	9.62	0.0633	0.419	6.61	0.6874	6.04
	Standard deviation		0.27	0.05		0.26	0.07	0.007	0.17
	Coefficient of variation (%)		0.52	0.52		1.03	1.01	1.06	2.75
2	Ni–Ni-4	497.5	48.96	10.16	0.0377	0.26	6.99	0.6884	6.21
	Ni–Ni-5	497.5	48.69	10.22	0.0372	0.26	7.01	0.6861	6.17
	Ni–Ni-6	497.5	49.07	10.14	0.0372	0.26	6.99	0.6894	6.23
	Ni–Ni-7	497.5	49.23	10.11	0.0373	0.26	6.92	0.6848	6.11
	Ni–Ni-8	497.5	48.74	10.21	0.0367	0.25	6.93	0.6785	5.99
	Average		48.94	10.17	0.0372	0.26	6.97	0.6854	6.14
	Standard deviation		0.23	0.05		0.19	0.04	0.004	0.10
	Coefficient of variation (%)		0.46	0.46		1.25	0.63	0.63	1.57

A.2 Results of the study of the device constants of the electrolytic enrichment method using solid polymer electrolytes

Electrolytic enrichment was performed with a solid polymer electrolyte using HTO with a known concentration. Electrolytic enrichment (1,000 mL to ~70 mL) was performed with an electrolytic current of 50 A to investigate the tritium enrichment ratio (the device constant$Z = Tf/Ti$) and its variation. The results are shown in Table A.3. The mean value of the device constant Z was 8.42, and the coefficient of variation was approximately 2%. The tritium residual rate$R$ was calculated from the approximate volume enrichment ratio (1,000 mL to approximately 70 mL), and the device constant Z was approximately 0.59.

Table A.3 Electrolytic enrichment results for known HTO concentrations

Experiment No.	*Vi* (g)	*Ti* (Bq/L)	*Tf* (Bq/L)	*Z* (*Tf*/*Ti*)	*R*
1	1,000.00	11.494	93.47	8.132	Approx. 0.57
2	1,000.00	11.494	97.13	8.450	Approx. 0.59
3	1,000.00	11.494	96.67	8.410	Approx. 0.59
4	1,000.00	11.494	97.19	8.456	Approx. 0.59
5	1,000.00	11.494	99.13	8.624	Approx. 0.60
				Average 8.41 Standard deviation 0.18 Coefficient of variation (%) 2.1	Average approx. 0.59

A.3 Results of a study on the memory effect of the electrolytic enrichment method using solid polymer electrolytes

The memory effect between samples due to electrolytic enrichment with solid polymer electrolytes was investigated. After the electrolysis of HTO of a known concentration, the inside of the apparatus was electrolytically cleaned with 300 mL purified water (twice) and 300 mL background water (once) for tritium analysis. Then, the background water was electrolytically enriched (1,000 mL → approximately 70 mL) twice to obtain the tritium concentration in these two samples. The results are shown in Table A.4. In the table, " ± " represents the standard uncertainty ($k = 1$) associated with counting.

Table A.4 Measurement results of memory effect in the device

	Tritium concentration (mBq/L)
1st	73±18
2nd	*(50±18)

*: Below the lower detection limit

A.4 Introduction to an electrolytic enrichment device

This section describes the electrolytic tritium enrichment device developed by the Isotope Hydrology Section of the International Atomic Energy Agency (IAEA). This device was installed by the Fukushima Prefectural Centre for Environmental Creation as part of an IAEA cooperation project.[108,109] Figure A.2 shows the schematic of the device. The device has the following characteristics.

- The anode is stainless steel, and the cathode is mild steel. They are treated with acid before use.
- Able to process sample volumes up to 2 L
- Maximum current value is 10 A
- Antifreeze is used in cooling water to maintain the temperature at 0.5°C
- Liquid volume after enrichment is 12–20 mL
- After enrichment, neutralization by bubbling carbon dioxide and distillation are possible.
- Power supply requires conversion due to foreign specifications
- A lower detection limit of 0.006 Bq/L can be achieved[110]

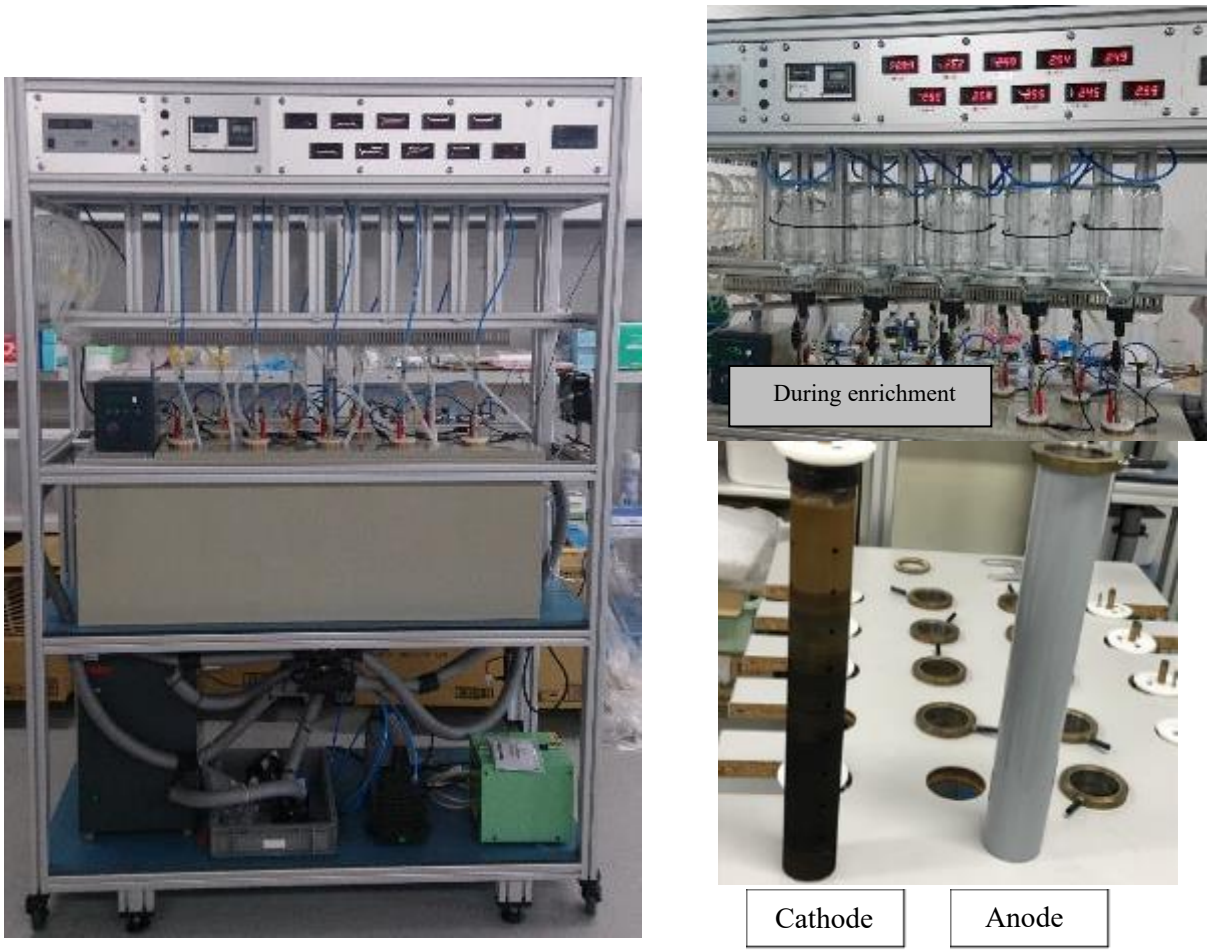


Figure A.2 Photographs of the device and electrodes

[108] Photographs and analysis data were provided by the Fukushima Prefectural Centre for Environmental Creation.

[109] Similar equipment can be purchased from domestic manufacturers.

[110] B. Kumar et al.: A Compact Tritium Enrichment Unit for Large Sample Volumes with Automated Re-Filling and Higher Enrichment Factor. *Appl. Radiat. Isot.*, **118**, 80-86, (2016).

The results for the enrichment of HTO of a known concentration obtained using this device are shown below.

Table A.5 Analytical conditions

Sample volume	1,000 mL
Sample volume after enrichment	15–20 mL
Maximum current value	7.5 A
Integrated current value	2,913.7 Ah
Enrichment period	~17 days
Sample cooling temperature	~0°C
Measurement method	Liquid scintillation counter
Emulsified scintillator	Ultima Gold LLT
Sample : Scintillator	10 mL : 10 mL
Measurement time	500 min

Table A.6 Analysis results

No.	Sample volume Vi (mL)	Sample volume after enrichment Vf (mL)	Volume enrichment ratio N	Concentration before enrichment Ti (Bq/L)	Concentration after enrichment Tf (Bq/L)	Enrichment ratio Z	Residual ratio R
1	999.50	17.28	57.84	10.2	485.9	47.64	0.824
10	999.69	15.37	65.04	10.2	547.0	53.63	0.825

Explanation B Calculation of Absolute Humidity

The specific radioactivity (Bq/g) of samples collected using the methods described in 3.2.3 Method using a dehumidifier and 3.2.4 Passive method is measured. To calculate the tritium concentration in air, it is necessary to separately determine the amount of water per unit volume in air, i.e., absolute humidity (g/m^3). The value measured using a hygrometer is relative humidity, expressed as a percentage of the maximum amount of water vapor that can be contained in air at a given temperature. Therefore, water vapor pressure (the pressure that water vapor accounts for in the total air pressure) is determined from relative humidity and saturated water vapor pressure (the pressure of water vapor when air contains the maximum amount of water vapor), and the absolute humidity is calculated from the gas state equation.

B.1 Calculation of saturated water vapor pressure

Using the saturated water vapor pressure equation, saturated vapor pressure is determined from the average value of the temperature during the sampling period. The saturated vapor pressure equation is not universal, and various equations are used for this purpose. However, differences between them are negligible compared to the uncertainty of the equation and measurement; therefore, it is not a practical problem[111]. The following is an example of the Sonntag's formula, as adopted from JIS Z 8806:2001 "Humidity - Measurement Methods"[112].

$$\ln(e_w) = -6096.9385 \times T^{-1} + 21.2409642 - 2.711193 \times 10^{-2} \times T + 1.673952 \times 10^{-5} \times T^2 + 2.433502 \times \ln(T)$$

where

e_w : Saturated vapor pressure of water (Pa)

T : Average absolute temperature (K) over the sampling period

B.2 Calculation of water vapor pressure

Determine water vapor pressure from the average relative humidity over the sampling period and saturated water vapor pressure of water determined in B[111,112,113].

$$e = \frac{e_w \times U_w}{100}$$

where

e : Water vapor pressure (Pa)

U_w : Average relative humidity (%) over the sampling period

e_w : Saturated water vapor pressure (Pa)

B.3 Calculation of the absolute humidity and volume of sampled air

The absolute humidity (g/m^3) is obtained by substituting the average value of temperature during the sampling period and water vapor pressure obtained in B.2 into the gas state equation.

Because the absolute humidity is the amount of moisture per unit volume in the atmosphere, it can be expressed by the following equation.

---

111 北野寛:日本における国家計量標準とその供給体制：湿度標準, *計測と制御*, **48(4)**,346-348 (2009).

112 JIS Z 8806:2001. Humidity - Measurement Methods.

113 芝亀吉：湿度とその測定法, *高分子*, **7(1)**, 53-56 (1958).

$$d_v = \frac{w}{V}$$

From the state equation for an ideal gas[114] $pV = \frac{w}{M}RT$, the absolute humidity is obtained by the following equations[115,116].

$$d_v = \frac{w}{V} = \frac{M \times p}{R \times T} = \frac{18 \times e}{8.31447 \times T}$$

where

d_v : Absolute humidity (g/m^3)
p : Pressure (Pa)
e : Water vapor pressure (Pa)
V : Volume (m^3)
w : Weight (g)
M : Molecular weight (g/mol)
R : Gas constant (8.31447 [(Pa·m^3)/(K·mol)])
T : Average absolute temperature (K) over the sampling period

[114] Because the subject here is the atmosphere at normal temperature and pressure, it was approximated as an ideal gas.
[115] JIS Z 8806:2001. Humidity - Measurement Methods.
[116] 芝亀吉：湿度とその測定法，高分子, 7(1), 53-56 (1958).

Explanation C Study on the Vacuum Freeze Drying of Biological Samples

Vacuum freeze drying is a time-consuming process in tritium analysis. A study explored[117] methods that reduce this treatment process. In this report, the authors show that by reducing the size of the frozen sample mass and increasing the surface area in vacuum freeze drying, they quickly realize a constant sample weight, specifically, the weight of 200 g frozen sample became constant in four days.

When preparing samples for TFWT and OBT from marine organisms via vacuum freeze drying, ~2 kg frozen samples, including spare samples, is required. To obtain a constant weight, vacuum freeze drying this amount of the sample as a single frozen mass takes approximately 2–3 weeks.

Therefore, investigation was conducted into accelerating the process by increasing the surface area of the frozen sample, as described below.

C.1 Study Method

1) A total of 12 samples was selected from 6 marine species (2 samples each).
2) The muscle was separated, chopped, and 1 kg sample was flattened. Further, the sample was placed in a thick plastic bag and frozen. Another 1 kg sample was divided into five portions, flattened, placed in separate thick plastic bags (0.2 kg x 5 bags), and frozen.
3) Each frozen sample was placed in a stainless steel drying container (each of the five divided samples was placed so that they did not overlap) and dried using the vacuum freeze dryer.
4) The number of days required for freeze drying (days to reach a constant weight) was measured for the single frozen flat sample and for samples divided into five portions.

In this study, 1 kg sample placed in a stainless steel drying container was considered to have a constant weight when the difference from the weight measured on the previous day was 1 g or less (the stainless steel drying container containing the sample was removed from the manifold, and the weight was measured).

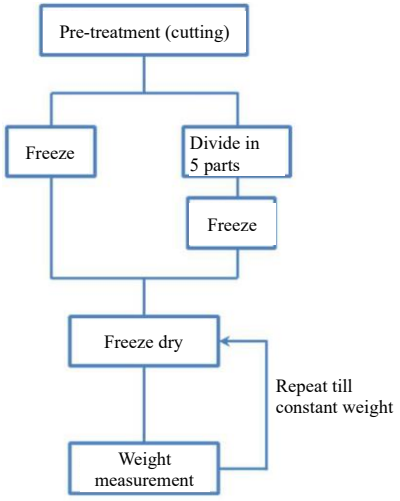


Figure C.1 Treatment process

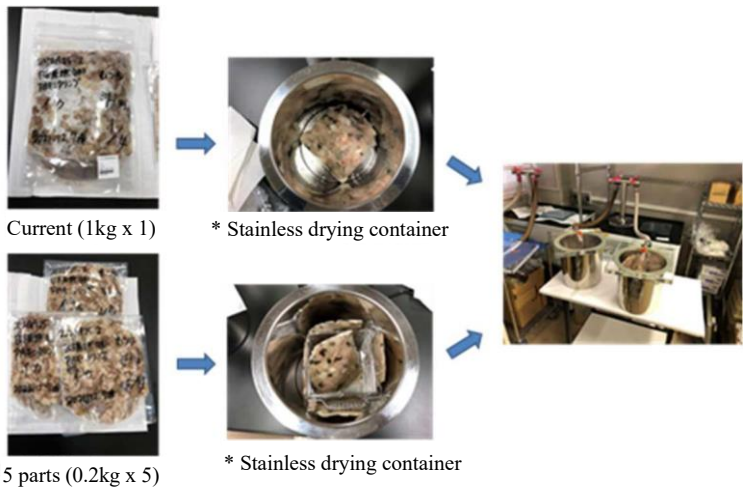


Figure C.2 Treatment process (photo)

C.2 Investigation Results

[117] H. Kuwata et al., Rapid Tritium Analysis for Marine Products in the Coastal Area of Fukushima. *Radiat. Environ. Med.*, **9(1)**, 28-34 (2020).

The number of days required for freeze drying (the number of days needed to reach a constant weight) for the single frozen sample and sample divided into five portions were 9 and 5 days, respectively (Figure C.3), confirming that efficient freeze drying can be achieved by increasing the surface area.

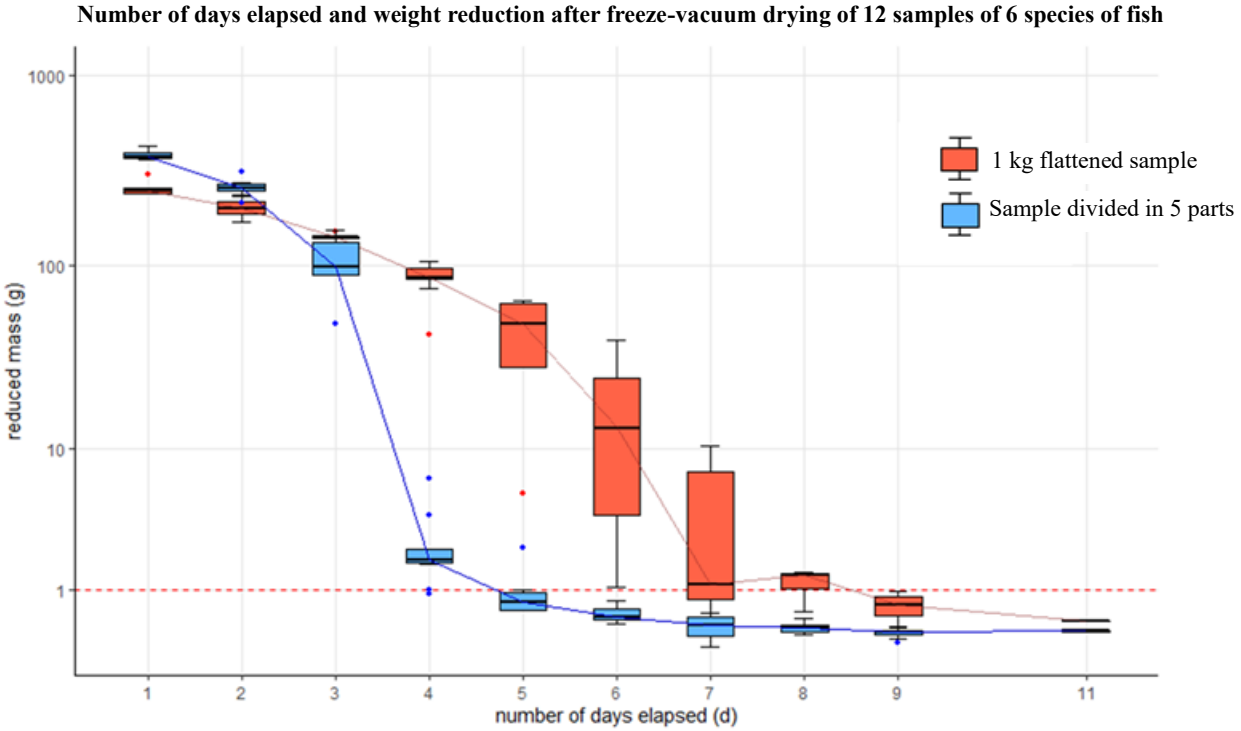


Figure C.3: Number of days elapsed and the corresponding observed weight loss

* The range of boxes indicates the first quartile to the third quartile, and the line within the box denotes the median. Points outside the box indicate outliers.

Explanation D Results of Investigation and Review of Commercial Emulsified Scintillators and Measuring Containers

Typical emulsified scintillators used for performing environmental tritium concentration measurements were compared in terms of their characteristics such as the background counting rate and counting efficiency. In addition, the effects of differences in material on counting efficiency and fluctuations in background counting rates were compared for several types of measuring containers, and the optimal combination of the emulsified scintillator and measuring container for low-tritium-concentration measurements was investigated.

(1) Commonly used commercial emulsified scintillators and their main characteristics

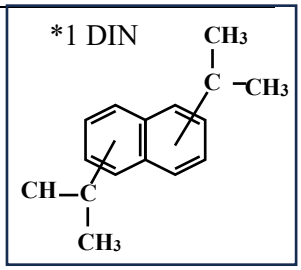
Typical commercial emulsified scintillators currently used for tritium measurements and their characteristics are listed in Table D.1. This information is taken from catalogs and Safety Data Sheets (SDS). They are all characterized by low background, high counting efficiency for tritium, and high sample retention in water. The main characteristics of emulsified scintillators are listed below.

1) Solvents used include pseudocumene (PC), di-isopropyl naphthalene (DIN), and phenyl xylyl ethane (PXE).
2) Flash points are broadly classified into two groups: those with flash points ranging from room temperature to approximately 50°C and those with flash points ranging from 140°C to 160°C. This is because this parameter depends on the nature of the solvent used.
3) The mixture ratio with water is often approximately 40%–60%, and it is measured in a single-phase liquid form.
4) When the measurement sample is prepared by mixing with water, heating is required if the emulsified scintillator in the gel form is used, but when the scintillator is a single-phase liquid, heating is not necessary and only shaking is required.

Table D.1 Main properties of commercial emulsified scintillators (data taken from catalogs and SDSs)

	Ultima Gold LLT	Ultima Gold uLLT	Ultima Gold XR
Solvent	Di-isopropyl naphthalene: DIN[*1]		
Freezing point (°C)	No data	No data	No data
Boiling point (°C)	290°C	290°C	290°C
Flash Point (°C)	140°C	140°C	152°C
Ignition point (°C)	500°C	500°C	350°C
Vapor pressure (hPa, at 25°C)	No data	N.A.	1.3 hPa
Density (hPa, at 20°C)	0.98	0.98	1.005
Sample retention	~54%	~54%	~50%
Sample condition at maximum retention	Single-phase liquid	Single-phase liquid	No data
Characteristics	• Biologically degradable • High flash point • No diffusion through polyethylene vial walls • Can be measured without distillation	• Eliminates background due to ^{40}K • High flash point	• No diffusion through polyethylene vial walls • Dispensable outside fume hood
Toxic substance	2-(2-Butoxyethoxy) ethanol[*2,3] Polyoxyethylene nonylphenyl ether[*4]	Diethylene glycol monobutyl ether[*2,3] Polyoxyethylene nonylphenyl ether[*5]	Polyoxyethylene nonylphenyl ether[*5]
Remarks	No LD data	No LD data	[Oral] Rat • Sodium 1,4-bis [(2-ethylhexyl)oxy]-1,4-dioxobutane-2-sulfonate LD50 = 4,200 mg/kg • Triethyl phosphate LD50 = 1,131–1,600 mg/kg

	Ecoscint Ultra	Aqualight+ Ultralow Level
Solvent	Di-isopropyl naphthalene: DIN[*1]	
Freezing point (°C)	−30°C	No data
Boiling point (°C)	290°C	No data
Flash Point (°C)	93°C	140°C
Ignition point (°C)	No data	No data
Vapor pressure (hPa, at 25°C)	No data	No data
Density (hPa, at 20°C)	0.96	No data
Sample retention	~50%	~55 %
Sample state at maximum retention amount	Single-phase liquid	Single-phase liquid
Characteristics	• Suitable for ultralow-level count measurements • Low toxicity	• Suitable for urine samples and samples with high mineral concentrations
Toxic substance	Bis(1-methylethyl)naphthalene[*6] Butyl Dioxitol[*6] Linear alkyl phenyl ethoxylates[*6]	Nonylphenol ethoxylate[*7]
Remarks	No LD data	No LD data



*2 Ingredients falling under "Hazardous substances subject to labeling" in the Industrial Safety and Health Act

*3 Ingredients falling under "Hazardous substances subject to notify" in the Industrial Safety and Health Act

*4 Ingredients falling under the "Class 1 Designated Chemical Substances" in the Act on the Assessment of Releases of Specified Chemical Substances in the Environment and the Promotion of Management Improvement

*5 Ingredients falling under the "Designated Chemical Substances" in the Act on the Assessment of Releases of Specified Chemical Substances in the Environment and the Promotion of Management Improvement

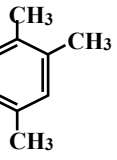
*6 Substances classified into hazard categories in the Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

*7 Substances subject to authorization under the REACH Regulation

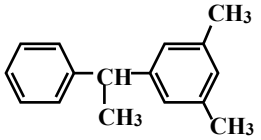
	Ecoscint XR	Ecoscint A	Insta Gel Plus	Pico-Fluor Plus
Solvent	Phenyl Xylyl Ethane: PXE[*1]		1,2,4-trimethylbenzene Also known as Pseudocumene: PC[*2]	
Freezing point (°C)	0°C	0°C	No data	No data
Boiling point (°C)	302°C–318°C	302°C–318°C	170°C	No data
Flash Point (°C)	91°C	74°C	48°C	50°C
Ignition point (°C)	375°C	No data	200°C	No data
Vapor pressure (hPa, at 25°C)	No data	No data	3 hPa	3 hPa
Density (hPa, at 20°C)	0.91	0.98	0.96	0.93
Sample retention	~50%	~28%	~50%	~28%
Sample state at maximum retention	Single-phase liquid	No data	Liquid to gel phase (depending on the sample volume)	Two-phase liquid
Characteristics	• High flash point • Excellent biodegradability • Suitable for samples with a wide range of pH values and high salt concentrations	• Strong inhibitory effect on photoluminescence and chemiluminescence	• Explosion range: 1.1–7.0 vol%. • Suitable for water-soluble and fat-soluble samples • Powders and solids can be measured in the gelation region	• pH6.0–7.0 • Suitable for samples that dissolve in nonpolar organic solvents
Toxic substance	Phenyl xylyl ethane[*3], linear alkyl phenyl ethoxylates[*3], primary alcohol ethoxylate[*3], and butoxy ethanol[*3]	Phenyl xylyl ethane[*3], Linear alkyl phenyl ethoxylates[*3], and methanol[*3],	1,2,4-trimethyl-benzene[*4,5] and polyoxyethylene nonylphenyl ether[*6]	1,2,4-trimethyl-benzene[*4,5], polyoxy-1,2-ethanediyl*[6], and diethylene glycol monobutyl ether[*4,5]
Remarks	[Oral] Rat LD50 > 1,500 mg/kg	No LD Data	[Oral] Rat 1,2,4-trimethylbenzene LD50 = 5,000 mg/kg	[Oral] Rat 1,2,4-trimethylbenzene LD50 = 5,000 mg/kg

	Hydrofluor	MonoFluor
Solvent (content)	Solvent Naphtha, Light Aromatic：SN	
Freezing point (°C)	0°C	0°C
Boiling point (°C)	182.2°C	182.2°C
Flash Point (°C)	31°C	50°C
Ignition point (°C)	463°C	463°C
Vapor pressure (hPa, at 25°C)	2.7 hPa	2.7 hPa
Density (hPa, at 20°C)	0.92	0.92
Sample retention	~33%	~33%
Sample condition at maximum retention	Gel phase	Single-phase liquid
Characteristics	• Methanol 2%–5% • Up to 15% liquid phase • 15%–25% two phases • 25%–50% gel phase (A two-phase sample is not suitable for measurement)	• Primary alcohol ethoxylate 5%–10% • Alkyl phenol ethoxylate 30%–40% • Butanol 1%–5%
Toxic substance	Solvent naphtha, light aromatic[*3], and methanol[*3]	Solvent naphtha, light Aromatic[*3], primary alcohol ethoxylate[*3], linear alkyl phenyl ethoxylates[*3], and butoxy ethanol[*3]
Remarks	No LD data	No LD data

*1 PXE



*2 PC



*3 Three Substances classified into hazard categories in the Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

*4 Ingredients falling under "Hazardous substances subject to labeling" in the Industrial Safety and Health Act

*5 Ingredients falling under "Hazardous substances subject to notify" in the Industrial Safety and Health Act

*6 Ingredients falling under "Designated Chemical Substances" in the Act on the Assessment of Releases of Specified Chemical Substances in the Environment and the Promotion of Management Improvement

(2) Study on the performance index of commercial emulsified scintillators

Tritium standard samples and background samples prepared using commercially available emulsified scintillators (11 types) were analyzed (20 mL glass vials were used as the measuring container) using an LSC, with the measurement conditions corresponding to each scintillator set according to those provided in 5.3.1 Setting the measurement conditions based on the figure of merit (FOM), and the FOMs were compared. In principle, the water content was assumed to be 50% (10 mL sample + 10 mL emulsified scintillator), but for scintillators with a catalog value of less than 50%, the water content was determined by referring to the catalog values of the corresponding emulsified scintillators and adding the emulsified scintillator to prepare a total volume of 20 mL.

The results are shown in Table D.2. The FOM was the highest for Ecoscint Ultra at 50% water content, followed by Ultima Gold uLLT.

Table D.2 FOM of various emulsified scintillators

Scintillator name	Solvent	Water content (mL)	Counting efficiency (%)	BG (cpm)	Figure of merit* (FOM)
Ultima Gold LLT	DIN	12	26.1	8.98	7.59×10^3
Ultima Gold uLLT	DIN	12	27.7	9.97	7.70×10^3
Ultima Gold XR	DIN	10	23.7	9.25	6.06×10^3
Ecoscint Ultra	DIN	10	28.9	9.78	8.54×10^3
Aqualight+ Ultralow Level	DIN	12	26.6	9.34	7.57×10^3
Ecoscint XR	PXE	10	17.8	6.88	4.60×10^3
Ecoscint A	PXE	4	45.9	12.31	4.27×10^3
Insta Gel Plus	PC	10	25.3	8.64	7.41×10^3

Pico-Fluor Plus	PC	4	33.9	8.46	3.40×10^3
Hydrofluor	SN	5	38.7	10.94	3.42×10^3
MonoFluor	SN	5	35.0	11.41	2.69×10^3

* Figure of merit = (Water content (mL) x Counting efficiency (%))^2/BG (cpm)

(3) Considerations regarding measurement containers

Tritium standard and background samples (Ultima Gold LLT was used as the scintillator) prepared using six types of measuring containers made of different materials were measured as above, and their FOMs were compared.

The results of the study of FOMs are shown in Table D.3. Background counting rate tended to be higher for glass. The FOM was of the order of 10^5 for the 145 mL polyethyleneand 100 mL fluoroplastic containers, compared to the order of 10^4 for the 20 mL polyethylene container and 10^3 for the 20 mL glass container, respectively.

Table D.3 Performance index by each measuring container

Material	Capacity (mL)	Water content (mL)	Counting efficiency (%)	BG (cpm)	Figure of merit* (FOM)	Remarks
Glass	20	10	26.1	8.98	7.59×10^3	Made of low-potassium borosilicate glass
	20	10	24.3	9.82	6.02×10^3	Made of low-potassium borosilicate glass UV transmittance ≥ 90 % Thickness: 0.9 mm Heat resistance temperature: 100°C
Polyethylene	20	10	24.2	1.27	4.63×10^4	Made of high-density polyethylene Thickness: 1mm Heat resistance temperature: 80°C
	20	10	28.0	1.10	7.13×10^4	Fluoroplastic coating on the inside of vials Thickness: 1mm Heat resistance temperature: 80°C

	145	70	20.1	3.14	6.29×10^5	Fluoroplastic coating on the inside of vials
Fluoropolymer	100	50	23.7	4.59	3.39×10^5	Chemically inert against organic solvents

* Figure of merit = (water content (mL) x counting efficiency (%))^2/BG (cpm)

Explanation E Data Rejection Test

E.1 Grubbs' Test

This method is used to test the presence of outliers in data that appear to follow a normal distribution. Outliers here are strictly in the statistical sense, i.e., values that are isolated from the rest of the population. Note that this does not necessarily mean that there was something wrong with the sample or analytical operation.

Let the data be $C_1, C_2, \cdots, C_n$. Test the maximum C_{max} or minimum C_{min} using the mean $\bar{C}$ and variance V of the data.

First, the mean $\bar{C}$ and variance V are obtained using the following equation.

$$\bar{C} = (C_1 + C_2 + \cdots + C_n)/n$$

$$V = \sum_{i=1}^{n} (C_i - \bar{C})^2/(n-1)$$

For testing the maximum value C_{max},

$$T = (C_n - \bar{C})/\sqrt{\mathrm{V}}$$

is used.

Additionally, for testing the minimum C_{min},

$$T = (\bar{C} - C_1)/\sqrt{\mathrm{V}}$$

is used. Compare this T with the value $G(n;\alpha)$ listed in Table E.1, and if $T > G(n;\alpha)$, confirm that it is an outlier with a risk factor of α.

(Example 1) Measurement was repeated 10 times, yielding the following values.

i	1	2	3	4	5	6	7	8	9	10
x_i	193	227	239	226	254	217	208	204	209	182

Verify whether the maximum value 254 is an outlier.

The mean $\bar{C} = 215.9$, variance $V = 459.66$, and maximum $C_{max} = 254$, $T = 1.777$, and $G(10,0.05) = 2.176$. Therefore, it cannot be considered significant with the risk factor of $0.05(5\ \%)$.

Test whether the minimum value 182 is an outlier.

The mean $\bar{C} = 215.9$, variance $V = 459.66$, and minimum $C_{min} = 182$, $T = 1.581$, and $G(10,0.05) = 2.1176$ are obtained. Therefore, it cannot be considered significant with the risk factor of $0.05(5\ \%)$.

Table E.1 Rejection limits for the Grubbs' method $G(\eta;\alpha)$

$Data$ count	$Upper\ significance\ level$ (χ)		$Data\ count$	$Upper\ significance\ level$ (χ)	
n	0.05	0.01	n	0.05	0.01
3	1.153	1.155	31	2.759	3.119
4	1.463	1.492	32	2.773	3.135
5	1.672	1.749	33	2.786	3.150
			34	2.799	3.164
6	1.822	1.944	35	2.811	3.178
7	1.938	2.097			
8	2.032	2.221	36	2.823	3.191
9	2.110	2.323	37	2.835	3.204
10	2.176	2.410	38	2.846	3.216
			39	2.857	3.228
11	2.234	2.485	40	2.866	3.240
12	2.285	2.550			
13	2.331	2.607	41	2.877	3.251
14	2.371	2.659	42	2.887	3.261
15	2.409	2.705	43	2.896	3.271
			44	2.905	3.282
16	2.443	2.747	45	2.914	3.292
17	2.475	2.785			
18	2.504	2.821	46	2.923	3.302
19	2.532	2.854	47	2.931	3.310
20	2.557	2.884	48	2.940	3.319
			49	2.948	3.329
21	2.580	2.912	50	2.956	3.336
22	2.603	2.939			
23	2.624	2.963	60	3.025	3.411
24	2.644	2.987	70	3.082	3.471
25	2.663	3.009	80	3.130	3.521
			90	3.171	3.563
26	2.681	3.029	100	3.207	3.600
27	2.698	3.049			
28	2.714	3.068			
29	2.730	3.085			
30	2.745	3.103			

E.2 Chi-square test

To examine whether a set of data follows a certain distribution, calculate the quantity χ^2 defined as follows.

$$\chi^2 = \sum_{i=1}^{n} \left(C_i - \bar{C}\right)^2 / \bar{C} \qquad (E.1)$$

where C_i is the i-th measured value, and assuming that measurement is repeated n times. $\bar{C}$ is the average total value, defined as follows:

$$\bar{C} = \sum_{i=1}^{n} C_i / n \qquad (E.2)$$

.

Table E.2 lists the values of the χ^2 distribution. There are $(v) = n - 1$ degrees of freedom. The value (P) in the top row of the table indicates the probability that the value of χ^2 exceeds the number in the table. For example, $P = 0.050$ means that the probability that the calculated χ^2 value exceeds the number in the table is5 %.

In other words, the probability of exceeding the values in Table E.2 is small and statistically unlikely to occur. As is clear from equation$(E.1)$, when the measured value deviates significantly from the average measured value $\bar{C}$, χ^2 becomes large. The fact that the value of χ^2 becoming a large value is statistically unlikely indicates that there may be a problem with the data.

Furthermore, if the χ^2 value is too small, the data spread will be too small, and data shall be questioned in this case as well.

(Example 2) Measurement was repeated 10 times, resulting in the following values.

i	1	2	3	4	5	6	7	8	9	10
C_i	193	227	239	226	254	217	208	204	209	182

From Equations $(E.1)$ and $(E.2)$,

$\bar{C} = 215.9$

$\chi^2_1 = 19.16 > \chi^2_{0.05}(9) = 16.92$

Because the χ^2_1 value exceeded the value in the table, calculation is performed again by excluding "254", which has the largest absolute difference between the average and count, for that, recalculate, and obtain following values;

$\bar{C} = 211.7$

$\chi^2_2 = 11.93 < \chi^2_{0.05}(8) = 15.50$

Therefore, the 5-th number 254 is rejected in this measurement.

Furthermore, as the χ^2_2 value is larger than that at $P = 0.975$, it can be concluded that data are sufficiently spread out.

Table E.2 χ^2 Distribution chart

ν \ P	0.995	0.975	0.050	0.025	0.010	0.005
1	0.043927	0.039821	3.84146	5.02389	6.63490	7.87944
2	0.010025	0.050636	5.99147	7.37776	9.21034	10.5966
3	0.071721	0.215795	7.81473	9.34840	11.3449	12.8381
4	0.206990	0.484419	9.48773	11.1433	13.2767	14.8602
5	0.411740	0.831211	11.0705	12.8325	15.0863	16.7496
6	0.675727	1.237347	12.5916	14.4494	16.8119	18.5476
7	0.989265	1.68987	14.0671	16.0128	18.4753	20.2777
8	1.344419	2.17973	15.5073	17.5346	20.0902	21.9550
9	1.734926	2.70039	16.9190	19.0228	21.6660	23.5893
10	2.15585	3.24697	18.3070	20.4831	23.2093	25.1882
11	2.60321	3.81575	19.6751	21.9200	24.7250	26.7569
12	3.07382	4.40379	21.0261	23.3367	26.2170	28.2995
13	3.56503	5.00874	22.3621	24.7356	27.6883	29.8194
14	4.07468	5.62872	23.6848	26.1190	29.1413	31.3193
15	4.60094	6.26214	24.9958	27.4884	30.5779	32.8013
16	5.14224	6.90766	26.2962	28.8454	31.9999	34.2672
17	5.69724	7.56418	27.5871	30.1910	33.4087	35.7185
18	6.26481	8.23075	28.8693	31.5264	34.8053	37.1564
19	6.84398	8.90655	30.1435	32.8523	36.1908	38.5822
20	7.43386	9.59083	31.4104	34.1696	37.5662	39.9968
21	8.03366	10.28293	32.6705	35.4789	38.9321	41.4010
22	8.64272	10.9823	33.9244	36.7807	40.2894	42.7956
23	9.26042	11.6885	35.1725	38.0757	41.6384	44.1813
24	9.88623	12.4001	36.4151	39.3641	42.9798	45.5585
25	10.5197	13.1197	37.6525	40.6465	44.3141	46.9278
26	11.1603	13.8439	38.8852	41.9232	45.6417	48.2899
27	11.8076	14.5733	40.1133	43.1944	46.9630	49.6449
28	12.4613	15.3079	41.3372	44.4607	48.2782	50.9933
29	13.1211	16.0471	42.5569	45.7222	49.5879	52.3356
30	13.7867	16.7908	43.7729	46.9792	50.8922	53.6720
40	20.7065	24.4331	55.7585	59.3417	63.6907	66.7659
50	27.9907	32.3574	67.5048	71.4202	76.1539	79.4900
60	35.5346	40.4817	79.0819	83.2976	88.3794	91.9517
70	43.2752	48.7576	90.5312	95.0231	100.425	104.215
80	51.1720	57.1532	101.879	106.629	112.329	116.321
90	59.1963	65.6466	113.145	118.136	124.116	128.299
100	67.3276	74.2219	124.342	129.561	135.807	140.169

E.3 K Sigma Test

K indicates the range of standard deviations, which is often 2 or 3. This is a method used for testing values in a series of values that show more variation than the statistical fluctuation. If an individual measurement differs by more than K times the standard deviation compared to the mean of the pair, the respective measurement is rejected as having a high probability of measuring a false pulse other than radiation (Figure E.1). The probability $P(K\sigma)$ that the absolute value of the difference between an individual measurement and the mean is greater than $K\sigma$ is shown in Table E.3 for a representative K value.

When $K = 2$, the probability of the measured value exceeding the average value $+2\sigma$ (or being less than the average value -2σ) is 5% or less $5\ \%$ and probability of it being more than the average value $+2\sigma$ (or less than the average value -2σ) due to statistical variations is extremely small. Conversely, fluctuations in the total value due to statistical fluctuations will fall within $95 \pm 2\sigma\ \%$.

Let C_i be the i-th measured value, and assume that measurement is repeated n times. Furthermore, when the distribution of possible values is assumed to be a normal distribution[118], the mean value ($\bar{C}$) and standard deviation (σ) are given by the following equations:

$$\bar{C} = \frac{1}{n}\sum_{i=1}^{n} C_i \qquad \text{(E. 3)}$$

[118] When assuming a Poisson distribution instead of a normal distribution, the mean ($\overline{C_{\text{poisson}}}$) and standard deviation ($\sigma_{poisson}$) are given by the following equations:

$$\overline{C_{\text{poisson}}} = \frac{1}{n}\sum_{i=1}^{n} C_i$$

$$\sigma_{poisson} = \sqrt{\overline{C_{\text{poisson}}}}$$

The Poisson distribution becomes closer to the normal distribution as the number of trials n increases. When the number of trials is 10 or more, equivalent results are obtained regardless of whether the distribution of measurements is assumed to be normal or Poisson. The Poisson distribution is better than the normal distribution with respect to accuracy. In addition, when assuming a normal distribution, there is a possibility that outliers cannot be rejected if the number of measurements is extremely small compared with the example; therefore, it is necessary to set the number of measurements and standard deviation appropriately.

$$\sigma = \sqrt{\sum_{i=1}^{n}(C_i - \bar{C})^2/(n-1)} \qquad \text{(E. 4)}$$

For each individual measurement, data that are $C_i > \bar{C} + K\sigma$ or $C_i < \bar{C} - K\sigma$ are rejected as outliers, and the average $\bar{C}$ is calculated again.

In the case of the K sigma test, if there is an outlier, the range of deviation expands. Therefore, it is preferable to perform a chi-square test before the K sigma test.

(Example 3)

Use the measurement results of E.2 (Example 2).

In this case, the fifth value, 254, was rejected by the χ^2 test.

i	1	2	3	4	5	6	7	8	9	10
C_i	193	227	239	226	(254)	217	208	204	209	182

The mean and standard deviation are calculated from the nine values as follows.

$\bar{C} = 212 \qquad \sigma = 17.76$

When $K = 2$, then $\bar{C} + 2\sigma = 247.5$ and $\bar{C} - 2\sigma = 176.5$, and there are no rejected measurements.

Table E.3 Probability of exceeding a certain deviation

K	1.00	1.64	1.96	2.00	3.00
$P(K\sigma)$	0.317	0.100	0.05	0.046	0.0026
Term	Standard deviation	90% error	95% error		

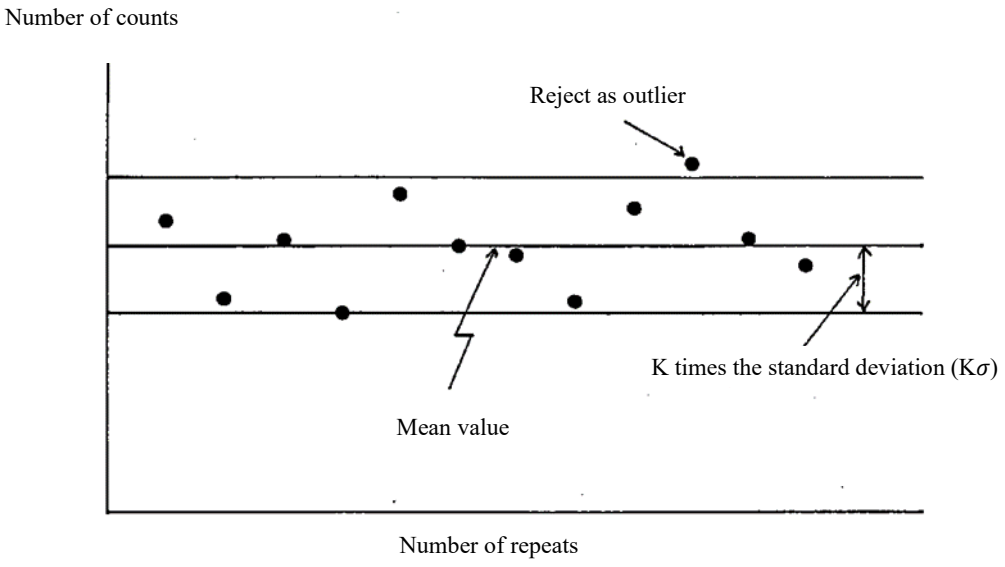


Figure E.1 Variation in measured values

Explanation F Example of Radioactivity Concentration Calculation

F.1 An example of tritium concentration calculation in the electrolytic enrichment method using metal electrodes[119]

An example of tritium concentration calculation using the electrolytic enrichment method with metal electrodes is shown below (Figure 2.7 Example of a record book for tritium electrolytic enrichment).

(1) Preparation of an alkaline electrolysis solution and the electrolysis cell

1) Weigh 2.53 g sodium peroxide into an Erlenmeyer flask with a stopper.

2) Add distilled sample water to prepare 505 g electrolyte.

505.00 g (Na_2O_2 + sample water)

3) Measure the weight of the glass cell, and designate it W1.

$W1 = 505.07$ g

4) Add 500 g prepared electrolyte to the glass cell, and designate it W2.

$W2 = W1 + 500.00\ \text{g} = 1005.07\ \text{g}$

5) Insert the metal electrode into it, measure the weight, and designate it W3.

$W3 = W2 + 397.83\ \text{g} = 1402.90\ \text{g}$

6) Weigh the total weight (glass cell + electrolyte + metal electrode) after electrolysis, and designate it $W4$.

$W4 = 962.69$ g

7) Perform the same operation for samples with a known tritium concentration.

(2) Calculation of the electrolytic enrichment ratio

8) Calculate the weight of the sample water before electrolysis.Vi[120]

$Vi = (W2 - W1) \times 0.995 = (1005.07 - 505.07) \times 0.995 = 497.5\ \text{g}$

9) Calculate the weight of enriched water after electrolysis Vf.

$Vf = Vi - (W3 - W4) = 497.5 - (1402.90 - 962.69) = 57.29\ \text{g}$

[119] This description is based on a sample water volume of 500.00 g and a measurement sample volume of 50.00 g. The amounts of test sample, measurement sample, and reagents and integrated current value can be changed appropriately depending on reaction conditions.

[120] If 505.00 g electrolyte is prepared by adding sample water to 2.53 g sodium peroxide, the ratio of sample water in the electrolyte is $(505.00 - 2.53)/505.00 = 0.995$.

10) Because integrated current required to electrolyze 1 g water is 2.98 Ah, the theoretical value (theoretical value of the weight of water to be electrolyzed) is calculated from the integrated current value actually flowed through the cell.

Integrated current value$= 1296.82$ Ah

Theoretical value $= 1296.82/2.98 = 435.17$ g

11) Calculate the difference between the weight of electrolyzed water (experimental value: $Vi - Vf$) and theoretical value to determine the amount of evaporation loss due to heat. An evaporation loss of approximately 5 g is usually observed.

$$\text{Experimental value} - \text{Theoretical value} = (Vi - Vf) - 435.17$$
$$= (497.5 - 57.29) - 435.17 \ = 5.04 \text{ g}$$

12) Calculate the volume enrichment ratio N.

$N = Vi/Vf = 497.5/57.29 = 8.68$

13) Calculate Vi, Vf and N in the same way for samples with known tritium concentrations.

$\text{STD} - 1$	$Vi = 497.5$ g	$Vf = 58.03$ g	$N = 8.57$
$\text{STD} - 2$	$Vi = 497.5$ g	$Vf = 57.49$ g	$N = 8.65$

14) The total radioactivity of the sample with the known tritium concentration before electrolysis is corrected for decay to the end date of electrolytic enrichment and calculated asTi × Vi. An example calculation for $\text{STD} - 1$ is shown below.

The amount of tritium in a part of the tritium standard solution Va g is

$Ti \times Va = 10.750$ Bq/g $\times$ 9.9790 g $= 107.27$ Bq

The amount of tritium in the electrolyte in the electrolysis cell Vb g is

$Ti \times Vb = 107.27$ Bq $\times (W2 - W1)/(\text{Na}_2\text{O}_2 + \text{sample water})$

$= 107.27 \times (1005.07 - 505.07)/505.00 = 106.21$ Bq

Decay coefficient[121] is given by $DF = 0.91098$

$Ti \times Vi = Ti \times Tb \times DF = 106.21 \times 0.91098 = 96.755$ Bq $(\text{STD} - 1)$

$Ti \times Vi = 96.136$ Bq $(\text{STD} - 2)$

15) Calculate the tritium concentration Ti in the sample with the known tritium concentration before electrolysis.

[121] The half life of tritium is set to 12.32 years during calculation.

$$Ti = (Ti \times Vi)/Vi = 96.755/497.5 \times 1000 = 194.48 \text{ Bq/kg } (\text{STD} - 1)$$

$$Ti = 193.24 \text{ Bq/kg } (\text{STD} - 2)$$

16) Measure the actual tritium concentration Tf[122] in the sample with the known tritium concentration after enrichment using an LSC.

$$Tf = 1224 \text{ Bq/L } (\text{STD} - 1)$$

$$Tf = 1244 \ Bq/L \ (STD - 2)$$

17) Calculate the tritium enrichment rate Tf/Ti.

$$Tf/Ti = 1224/194.48 = 6.29 \ (\text{STD} - 1)$$

$$Tf/Ti = 6.44 \ (\text{STD} - 2)$$

18) Calculate the tritium retention rate $\text{R} = (\text{Tf} \times \text{Vf})/(\text{Ti} \times \text{Vi})$.

$$R = (Tf \times Vf)/(Ti \times Vi) = 1224 \div 1000 \times 58.03/96.755$$

$$= 0.7341 \ (\text{STD} - 1)$$

$$R = 0.7439 \ (\text{STD} - 2)$$

19) Calculate the average value of R to calculate the tritium enrichment ratio F of the water sample.

$$\bar{R} = (0.7341 + 0.7439)/2 = 0.7390$$

$$F = N \times R = 497.5 \div 57.29 \times 0.7390 = 6.42$$

(3) Calculation of the tritium concentration

20) Calculate the tritium concentration in the sample after electrolysis.

$$\text{Tritium concentration after enrichment} = (1.6318 \pm 0.20096) \text{ Bq/L}$$

21) Divide by the tritium enrichment rate F[123], and correct for decay.

$$DF = 0.976557$$

Tritium concentration in analysed sample water

$$= (1.6318 \pm 0.20096)/F/DF$$

$$= (1.6318 \pm 0.20096)/6.42/0.976557$$

$$= (0.26028 \pm 0.03205) \text{ Bq/L}$$

---

[122] Since it is necessary to unify the decay correction date with that of the sample with known tritium concentration before electrolysis, the decay correction date is set to the end date of electrolysis.

[123] The tritium enrichment ratio F is calculated by multiplying the volume enrichment ratio N of the water sample by the tritium retention rate$R$ obtained from the radioactivity (Bq) ratio of the sample with the known tritium concentration before and after electrolysis, not the enrichment ratio of the sample with the known concentration.

F.2 Example of tritium concentration calculation using the electrolytic enrichment method with a solid polymer electrolyte[124]

(1) Prepare tritiated water of a known concentration (approximately 10 Bq/L).

1) Take $6.6413\ \mathrm{g}$ certified tritiated water measured $10.750\ \mathrm{Bq/g}\ at\ 2020/5/9$.

2) Add tritium-free water to dilute tritiated water to 6211.4 g.

3) Calculate the tritium concentration in the prepared tritiated water Ti as follows

$$Ti = 10.750 \times \frac{6.6413}{6211.4} \times 1000 = 11.494\ \mathrm{Bq/L}\ at\ 2020/5/9$$

4) Take $\mathrm{Vi} = 1000\ \mathrm{g}$ tritium water, and perform electrolytic enrichment.

(2) Determine the tritium concentration after electrolytic enrichment.

5) Subtract the background counting rate from the counting rate of enriched water obtained from the LSC to calculate the net counting rate.

Enriched water counting rate $= (69.27 \pm 0.3722)\ \mathrm{cpm}$

Background counting rate $= (3.958 \pm 0.06291)\ cpm$

Net counting rate $= (65.31 \pm 0.3775)\ \mathrm{cpm}$

6) Calculate the tritium concentration after enrichment from the net counting rate, counting efficiency, and measured sample volume.

Counting efficiency $= 25.60\ \%$

Measured sample volume $= 50.00\ \mathrm{mL}$

Tritium concentration after enrichment

$$= (65.31 \pm 0.3775)/25.60 \times 100/60/50.00 \times 1000$$

$$= (85.04 \pm 0.4915)\ \mathrm{Bq/L}$$

7) Correct the obtained tritium concentration Tf for enriched water for decay to the reference date (date of measurement)[125].

Date of measurement $= 2022/1/13$

Days elapsed $= 614\ \mathrm{days}$

Decay coefficient$DF = 0.9098$ is given by

$$Tf = (85.04 \pm 0.4915)/0.9098 = (93.47 \pm 0.540)\ \mathrm{Bq/L}$$

(3) Estimate the device constant $Z = Tf/Ti$.

---

[124] This description is based on a sample water volume of 1,000 g. The amount of sample, reagents, and integrated current value should be changed according to actual electrolysis conditions.

[125] The half life of tritium is set to 12.32 years during calculation.

8) Calculate the device constant Z from the calculated Ti and measured Tf.

$$Z = Tf/Ti = 93.47/11.494 = 8.132$$

9) Perform the above operations five times to obtain a series of Z values, and use the average value as the device constant.

(4) Calculate the tritium concentration in the analyzed water sample

10) Take $Vi = 1000\,\mathrm{g}$ distilled analyzed water sample, and perform electrolytic enrichment.

11) Calculate the tritium concentration in the water sample after enrichment using an LSC.

$$\text{Tritium concentration after enrichment} = (0.6172 \pm 0.1523)\ \mathrm{Bq/L}$$

12) Divide the obtained tritium concentration by the device constant Z to calculate the tritium concentration in the analyzed water sample.

$$\text{Tritium concentration in analysed sample water} = (0.6172 \pm 0.1523)/8.414$$
$$= (0.0734 \pm 0.0181)\ \mathrm{Bq/L}$$

Explanation G Evaluation of Uncertainty in Tritium Analysis

When performing tritium measurements on environmental samples, the quantity to be measured is radioactivity per unit (weight, volume, etc.) in samples, i.e., the radioactivity concentration. It is very difficult to estimate and completely define all conditions that affect the radioactivity concentration. In this context, it is nearly impossible to obtain the true value of the radioactivity concentration, and obtained measurement results, no matter how rigorously measurements and analyses are performed, are generally only the approximations or estimates of the true value of the radioactivity concentration. This imperfection also results in final measurement results exhibiting a certain range of variability.

In tritium measurements, the radioactivity concentration is not measured directly, but rather the number of scintillation emissions that reach the detector is counted when β-rays emitted by radionuclides to be measured interact with the scintillator. The result of the measurement, i.e., the radioactivity concentration, is calculated as a function of input quantities, such as the sample amount, detector counting efficiency, measurement time, and other correction factors, as well as the number of counts from the detector.

$$A = f(x_1, x_2, x_3, \cdots, x_n) = f(N, m, t, \varepsilon, \gamma, \cdots) \quad \text{(G.1)}$$

where

A : Radioactivity concentration

$f(x_1, x_2, x_3, \cdots, x_n)$: Function that represents calculations required to derive the radioactivity concentration

$N, m, t, \varepsilon, \gamma, \cdots$: Input quantities required to calculate the radioactivity concentration

The standard uncertainty of the radioactivity concentration to be determined is evaluated as the combined uncertainty of all input quantities involved in the calculation of the radioactivity concentration. If all input quantities are independent (uncorrelated), uncertainties of each input quantity are combined according to the following equation:

$$u(A) = \sqrt{\sum_{i=1}^{n} \left\{ \frac{\partial f}{\partial x_i} u(x_i) \right\}^2} \quad \text{(G.2)}$$

where

$u(A)$: Integrated standard uncertainty of the radioactivity concentration

$u(x_i)$: Standard uncertainty of input quantities $x_1, x_2, x_3, \cdots x_n$.

The differential coefficient $\partial f / \partial x_i$ in equation (G.2) is called the sensitivity coefficient. It describes changes in the output quantities A with variations in the respective values of input quantities $x_1, x_2, x_3, \cdots, x_n$. For example, the change in the output quantity A caused by a small change Δx_i in the input quantity x_i is calculated as $(\Delta A)_i = (\partial f / \partial x_i)(\Delta x_i)$. If this change is caused by the standard uncertainty of the input quantity x_i, then the corresponding change in the output quantity A will be $(\partial f / \partial x_i) u(x_i)$.

If the output quantity A is expressed only by the multiplication and division of input quantities $x_1, x_2, x_3, \cdots, x_n$, the relative standard uncertainty of the output quantity can be obtained by calculating the square root of the sum of the squares of the relative standard uncertainties of the respective input quantities. Thus, equation (G.2) becomes

$$\frac{u(A)}{A} = \sqrt{\sum_{i=1}^{n} \left\{ \frac{u(x_i)}{x_i} \right\}^2} \times 100\ (\%) \quad \text{(G.3)}$$

where

$u(A)/A$: Relative integrated standard uncertainty of the radioactivity concentration

$u(x_i)/x_i$: Relative standard uncertainty of input quantities $x_1, x_2, x_3, \cdots, x_n$

In this explanation, equation (G.3) is used to evaluate uncertainty.

G.1 Uncertainty Evaluation Procedure

Measurement uncertainty estimation is generally performed using the following procedure.

1) Determine factors that influence measurement results, and organize them as model equations for measurements.
2) Organize uncertainty factors based on model equations.
3) Evaluate uncertainty for individual uncertainty factors.

4) Combine all individual uncertainties to obtain the resultant uncertainty of measurements.

The procedure for uncertainty evaluation described above is outlined below.

1) Determine factors that influence measurement results, and organize them as model equations for measurements.

Factors that may affect the final measurement results must be determined as much as possible based on the measurement procedure and acceptance criteria via accuracy control and organized as model equations for measurements.

2) Organize uncertainty factors based on model equations.

The uncertainty factors associated with the quantification of the radioactivity concentration in tritium measurements can be divided into the following three major categories.

- Uncertainty associated with the analysis of samples
- Uncertainty associated with calibration and correction
- Uncertainty associated with the measurement of samples

Each category may have more detailed factors. Figure G.1 shows an example of an uncertainty factor diagram created to identify uncertainty factors. Note that there may be other factors besides those shown in Figure G.1 that affect the results of measurements.

3) Evaluate uncertainty for individual uncertainty factors.

Methods used for evaluating uncertainty are classified into two types: Type-A evaluation and Type-B evaluation.

Type-A evaluation is a method used for uncertainty evaluation based on the statistical analysis of a series of observed values. For each factor, the experimental standard deviation is obtained from repeated measurements and is used as the standard uncertainty.

Type-B evaluation is a method employed for evaluating uncertainty by means other than the statistical analysis of a series of observations. Here, each factor is evaluated by scientific judgement based on all available information regarding possible variability. Available information includes the following:

- Manufacturer specifications
- Data contained in calibration or other certificates
- Uncertainty assigned to reference data adopted from a handbook
- General knowledge or experience of the behaviors and properties of materials and measuring instruments

Not all uncertainty factors contribute considerably to the uncertainty of the measurement result being evaluated. After evaluating each uncertainty and combining uncertainties to determine their contribution to the overall uncertainty, items that contribute little can be omitted from evaluation in future measurements.

4) Combine all individual uncertainties to obtain the resultant uncertainty of measurements.

All individual uncertainties obtained in Step 3 are combined to yield the integrated standard uncertainty.

The integrated standard uncertainty obtained in Step 4 represents the standard deviation associated with the corresponding measurement result. If it is necessary to express an interval that is expected to contain measurement results, the coverage factor k is multiplied by the integrated standard uncertainty to obtain expanded uncertainty. k is determined from the level of confidence and $t-$distribution and is generally chosen between $2\sim3$. In the measurement of the radioactivity concentration, the distribution of measurement results can be regarded as a normal distribution; therefore, $k=2$ when the level of confidence is approximately 95%. When reporting measurement results, it is always necessary to clearly indicate the type of uncertainty listed alongside the measurement value (integrated standard uncertainty or expanded uncertainty ($k=2\sim3$)).

G.2 Uncertainty calculation procedure

G.2.1 Uncertainty associated with the analysis of samples

(1) Weighing (u_1)

Use the uncertainty value (uncertainty equation) stated in the calibration certificate. If the stated uncertainty is not a relative value, the relative standard uncertainty is calculated by the following formula:

$$u_1 = \frac{u(w)}{w} \quad \text{(G.4)}$$

where, $u(w)$: uncertainty of the weighing value (g) and w: weighing value (g)

If not stated in the calibration certificate, uncertainty due to rounding errors in the indicated values of the measuring instrument and that due to the accuracy of repeated measurements are each evaluated with reference to the following, and then they are combined to give the uncertainty of weighing.

1) Uncertainty due to rounding errors in indicated values

Let the reading limit (minimum scale) of the electronic balance be l. Then, the measured values are distributed rectangularly with $\pm l/2$ as the upper and lower limits for the zero point and weighing value. By combining these two distributions, a triangular distribution is obtained, with $\pm l$ as the upper and lower limits, which is used to calculate the relative standard uncertainty.

$$u_{1a} = \frac{l}{\sqrt{6}w} \quad \text{(G.5)}$$

where l: reading limit (g) and w: weighing value (g)

2) Uncertainty due to the accuracy of repeated measurements

For evaluation via repeated measurements, the weight of the measurement sample is measured approximately 10 times the same way as in normal measurements, and the average value and standard deviation are calculated. Then, the relative standard uncertainty is estimated using the following formula.

$$\frac{w_{STD}}{\overline{w}} \quad \text{(G.6)}$$

where $\overline{w}$: average value of repeated measurements (g) and w_{STD}: standard deviation of repeated measurements (g)

If the average value of n repetitions is adopted for measurements in actual operations, its standard uncertainty is given by

$$u_{1b} = \frac{w_{STD}}{\overline{w}} \times \frac{1}{\sqrt{n}} \quad \text{(G.7)}$$

n: number of repetitions

3) Combining weighing uncertainty

u_{1a} and u_{1b} are combined to obtain the relative standard uncertainty of weighing

$$u_1 = \sqrt{(u_{1a})^2 + (u_{1b})^2} \quad \text{(G.8)}$$

[Example of calculation]

If the value measured using the electronic balance with a minimum weighing capacity of $0.01\ g$ is $93.81\ g$,

$$u_{1a} = \frac{0.01}{\sqrt{6} \times 93.81} \times 100 = 0.0044\ \%$$

The results of repeated measurements are listed in G. 1,

Table G. 1 Repeated measurement result of weight

No.	1	2	3	4	5	6	7	8	9	10
Measured value (g)	93.78	93.81	93.82	93.8	93.81	93.8	93.81	93.81	93.82	93.81

Average of measured values:$93.807\ g$

Standard deviation:$0.0116\ g$

$$\frac{0.0116}{93.807} \times 100 = 0.012\ \%$$

Because a single measurement is usually employed when weighing samples,

$$u_{1b} = \frac{0.0116}{93.807} \times 100 \times \frac{1}{\sqrt{1}} = 0.012\ \%$$

Thus, the uncertainty of weighing is

$$u_1 = \sqrt{0.0044^2 + 0.012^2} = 0.013\ \%$$

G.2.2 Uncertainty associated with calibration and correction

In tritium measurements, changes in efficiency due to the quenching of the measurement sample must be considered. Therefore, it is necessary to create a quenching-correction curve using multiple tritium standard sources. The uncertainty to be considered when creating the quenching-correction curve is evaluated as follows.

(2) Uncertainty of standard sources (u_2)

Use uncertainty listed in the calibration source record.

(3) Weighing of standard sources (u_3)

[Example of calculation]

If the value measured using the electronic balance with a minimum weighing capacity of $0.0001\ g$ is $2.0012\ g$,

$$u_{3a} = \frac{0.0001}{\sqrt{6} \times 2.0012} \times 100 = 0.0020\ \%$$

When the results of repeated measurements are listed in Table G.2,

Table G.2 Repeated measurement result of weight

No.	1	2	3	4	5	6	7	8	9	10
Measured value (g)	2.0011	2.0013	2.0009	2.0013	2.0010	2.0012	2.0012	2.0014	2.0009	2.0012

Average of measured values:$2.0012\ g$

Standard deviation:$0.000172\ g$

$$\frac{0.000172}{2.0012} \times 100 = 0.0086\ \%$$

Because a single measurement is usually employed when weighing samples,

$$u_{3b} = \frac{0.000172}{2.0012} \times 100 \times \frac{1}{\sqrt{1}} = 0.0086\ \%$$

Thus, the uncertainty of weighing is

$$u_3 = \sqrt{0.0020^2 + 0.0086^2} = 0.0088\ \%$$

(4) Variations in measurement systems

Uncertainty due to fluctuations in the measurement system in the measurement period during calibration is considered small and negligible compared to other factors and is therefore omitted.

(5) Uncertainty from counting statistics (u_4)

The relative standard uncertainty is calculated from the number of counts obtained by measuring the standard source and statistical uncertainty of counts. The largest relative standard uncertainty calculated for each source is then used as the relative standard uncertainty of the correction curve.

$$u_4 = \frac{\sigma_{source}}{N_{source}} \quad \text{(G.9)}$$

where N_{source}: the number of counts from the source and σ_{source}: statistical uncertainty of counts

[Example of calculation]

The measurement of a standard source yields the results in Table G. 3.

Table G. 3 Measurement results for a calibration source

Quenching index value	Measurements (count)	Standard uncertainty related to counting	Relative standard uncertainty (%)
5.08	149,213	386.28	0.2589
4.57	150,506	387.95	0.2578
4.06	148,835	385.79	0.2592
3.57	142,810	377.90	0.2646
3.30	137,865	371.30	0.2693
3.03	131,359	362.43	0.2759
3.00	131,814	363.06	0.2754
2.90	129,017	359.19	0.2784
2.91	129,063	359.25	0.2784
2.73	104,546	323.34	0.3093

$$u_4 = 0.31\ \%$$

Note: If multiple sources are used for calibration, the maximum relative standard uncertainty of all quenching indices is used as the relative standard uncertainty of the correction curve.

(6) Calibration formula fitting (u_5)

From the calibration data of each standard source used for quenching calculation, the variation rate relative to actual measurement is calculated, and the largest of these values is taken as the relative standard uncertainty of the fitting of the calibration equation.

$$u_5 = f_{max} \quad \text{(G.10)}$$

where f_{max}: maximum value of the [variation rate relative to actual measurement]

[Example of calculation]

Efficiency calibration was performed using a calibration source, and the obtained results are listed in Table G. 4:

Table G. 4 Calibration data for each quenching index

Quenching index	Fitting value	Measured value	Variation rate relative to actual measurement (%)
5.08	30.90993	30.88683	−0.0748
4.57	31.13880	31.19801	0.1898
4.06	30.74496	30.70236	−0.1388
3.57	29.43643	29.46615	0.1009
3.30	28.45430	28.46671	0.0436
3.03	27.27467	27.24113	−0.1231
3.00	27.14267	27.09100	−0.1907
2.90	26.55155	26.57039	0.0709
2.91	26.62126	26.62385	0.0097
2.73	25.57643	25.61416	0.1473

$$u_5 = 0.19\ \%$$

(7) Decay correction (u_6)

Referring to the nuclear data used in analysis, the decay correction factors for the half life and half life + uncertainty are calculated for the time elapsed from the calibration date to the measurement date. Then, the relative value of the difference is taken as the relative standard uncertainty.

$$DF_1 = \left(\frac{1}{2}\right)^{\frac{t}{T}} \tag{G.11}$$

$$DF_2 = \left(\frac{1}{2}\right)^{\frac{t}{T+\sigma}} \tag{G.12}$$

$$u_5 = \frac{|DF_2 - DF_1|}{DF_1} \tag{G.13}$$

where T: half life, $T + \sigma$: half life + uncertainty, t: elapsed time,

DF_1: decay correction factor at T, and DF_2: decay correction factor at $T + \sigma$.

[Example of calculation]

The half life of tritium and its uncertainty DF_1 and DF_2, obtained by assuming that measurements are performed 60 days after the calibration date are shown in Table G.5. The nuclear data are adopted from the Evaluated Nuclear Structure Data File (ENSDF) (as of September 2022).

Table G.5 Half life of tritium and its uncertainty

Half life (year)	Uncertainty of half life (year)	DF_1	DF_2	Relative standard uncertainty (%)
12.32	0.02	0.990800	0.990815	0.0015

$$u_6 = 0.0015\ \%$$

G.2.3 Uncertainty associated with the measurement of samples

In tritium measurements, the radioactivity concentration is calculated by subtracting the counting rate of the measurement sample from the background counting rate to obtain the net counting rate and then applying quenching and half life corrections. Uncertainty considered in measurements is evaluated as follows.

(8) Uncertainty from counting statistics (u_7)

Same as uncertainty due to counting statistics in G.2.2 Uncertainty associated with calibration and correction (u_4). However, the net counting rate of an unknown sample is used in uncertainty calculation.

$$u_7 = \frac{\sigma_{sample}}{N_{sample}} \quad \text{(G.14)}$$

where N_{sample}: net counting rate of an unknown sample and σ_{sample}: statistical uncertainty of the counting rate.

(9) Variations in measurement systems (u_8)

A rectangular distribution, with the upper and lower limits as the acceptable variation range (relative value) set by the accuracy control, is assumed.

$$u_8 = \frac{Ac}{\sqrt{3}} \quad \text{(G.15)}$$

where Ac: upper limit of the acceptable variation range

If the variation in the measurement system is obtained by the accuracy control (trend chart), this value is assumed to be uncertainty.

[Example of calculation]

When the accuracy control is performed by measuring a reference source and acceptance criterion is set at ± 0.3 %,

$$u_8 = \frac{0.3}{\sqrt{3}} = 0.17\ \%$$

(10) Decay correction (u_9)

Same as the uncertainty of decay correction in G.2.2 Uncertainty associated with calibration and correction (u_6). As an example, assume that measurement was conducted 60 days after the collection date.

$$u_9 = 0.0015\ \%$$

Table G.6 Uncertainty budget sheet

Uncertainty factor	Relative standard uncertainty
Uncertainty associated with the analysis of samples	
Weighing	u_1
Uncertainty associated with calibration and correction	
Uncertainty of a standard source	u_2
Weighing of a standard source	u_3
Uncertainty due to counting statistics	u_4
Calibration formula fitting	u_5
Decay correction	u_6
Uncertainty associated with the measurement of samples	
Uncertainty due to counting statistics	u_7
Variations in measurement systems	u_8
Decay correction	u_9

Table G.7 Calculation example for an uncertainty budget sheet

Uncertainty factor	Relative standard uncertainty (%)
Uncertainty associated with the analysis of samples	
Weighing (u_1)	0.013
Uncertainty associated with calibration and correction	
Uncertainty of standard sources (u_2)	2.85
Weighing of standard sources (u_3)	0.00088
Uncertainty from counting statistics (u_4)	0.31
Calibration formula fitting (u_5)	0.19
Decay correction (u_6)	0.0015
Uncertainty associated with the measurement of samples	
Uncertainty from counting statistics (u_7)	Obtained from the counting results of the measured sample
Variations in measurement systems (u_8)	0.17
Decay correction (u_9)	0.0015
Relative combined standard uncertainty (Excluding the statistical uncertainty of counting u_7)	2.88

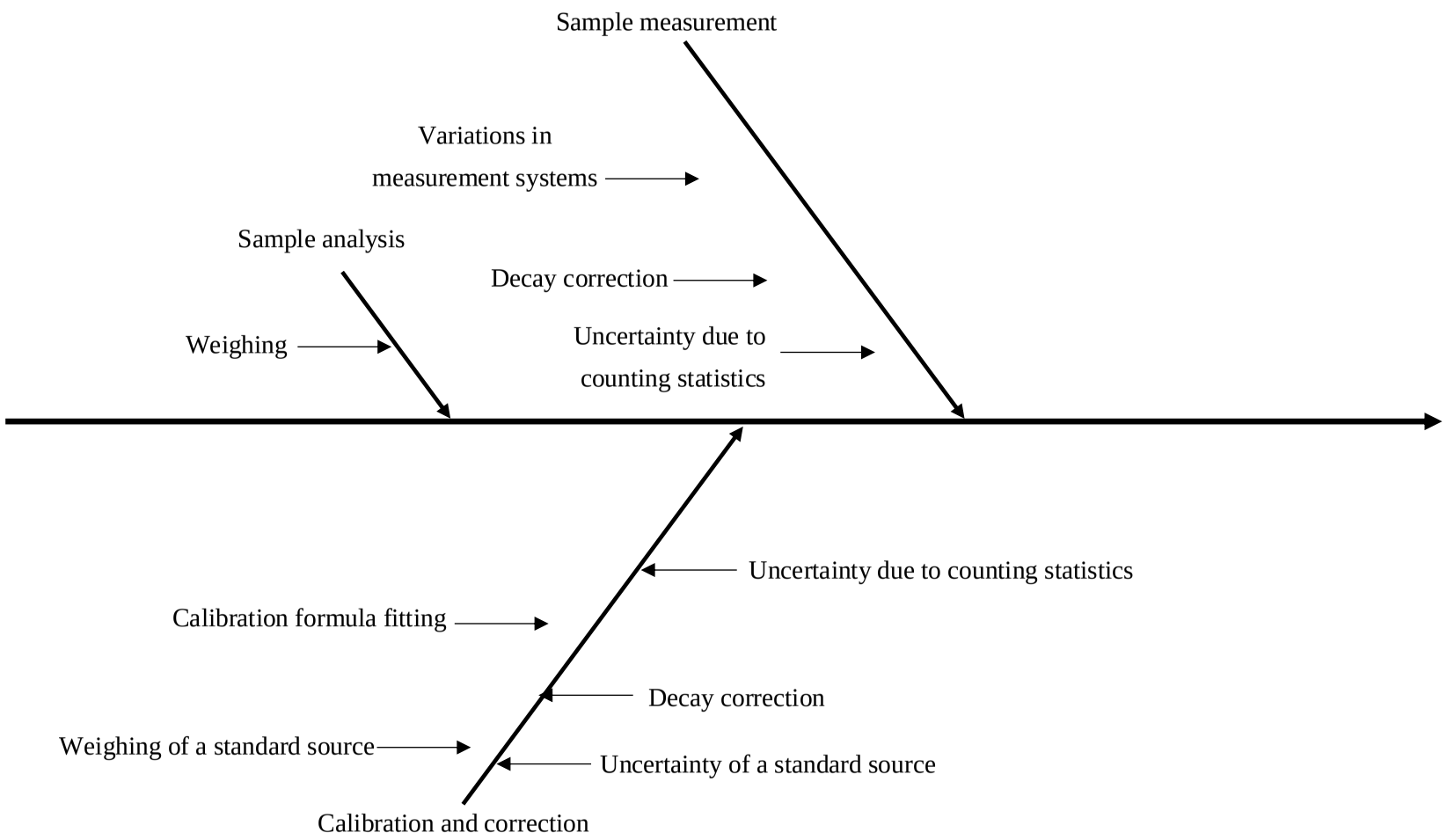


Figure G.1 Uncertainty factor diagram for tritium measurement (example)

Explanation H Calculation example of the lower detection limit

H.1 The lower detection limit according to ISO 11929

H.1.1 Concept

Regarding the lower detection limit, ISO 11929 introduces the concept of type-I and type-II errors for the distribution of background and measured values, respectively, and defines the decision threshold and lower detection limit. The detection limit is designed to handle uncertainty in the standard deviation of each distribution. In the Kaiser method, the standard deviation of the distribution of measured values is calculated using uncertainty associated with counting. However, for the lower detection limit according to ISO 11929, the standard deviation of the distribution uses the combined standard uncertainty of the measured quantity based on the ISO "Guide to the expression of Uncertainty in Measurement" (GUM).

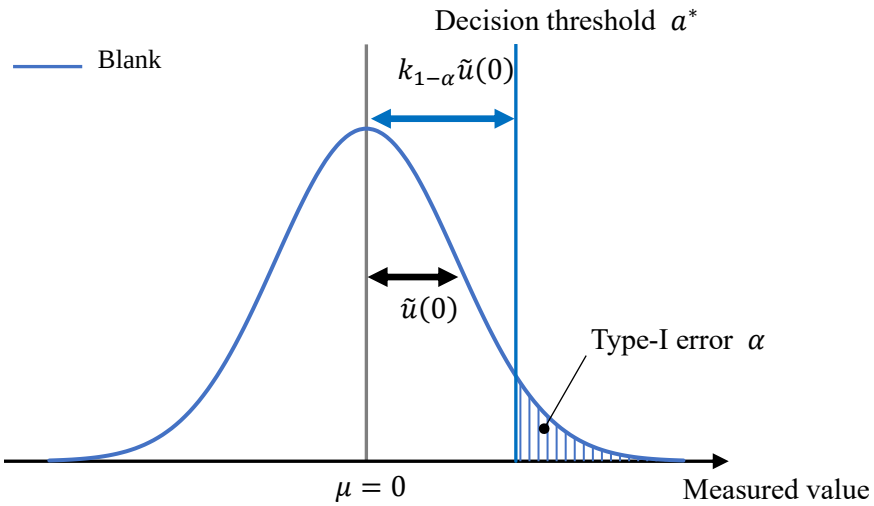
H.1.2 Decision threshold

The decision threshold is the value at which a physical effect is determined to be present and is defined by the distribution of blank measurements as follows. It is expressed by the following equation.

$$a^* = k_{1-\alpha} \times \tilde{u}(0)$$

*$\tilde{u}(0)$: uncertainty of the measured quantity when the best estimate is 0 (H.1)

In a background measurement that contains no radionuclides that are measured, the measured values will have a distribution similar to Figure H. 1 ($\mu = 0$). In this distribution, the measured value that exceeds the upper limit of the interval representing the confidence level $1 - \alpha$ (risk rate α) is the decision threshold, being a type-I error value that is significantly different from the blank and exhibiting a physical effect. In this case, the probability of the type-I error is α.



$\tilde{u}(0)$: uncertainty of the measured quantity when the best estimate is 0

$k_{1-\alpha}$: coverage factor for the confidence level of $1-\alpha$

Figure H. 1 Decision threshold

H.1.3 Lower detection limit

The lower detection limit is the value at which the measured value is attributed to the sample and not just to the blank and is defined as follows.

$$a^{\#} = a^* + k_{1-\beta} \times \tilde{u}(a^{\#}) \quad \text{(H.2)}$$

*$\tilde{u}(a^{\#})$: uncertainty of the measured quantity when the best estimate is $a^{\#}$

When the best estimate of the measured quantity in a sample measurement is greater than but close to the decision threshold, the measured values will have a distribution shown in Figure H. 2, which overlaps with the distribution of blank measurement.

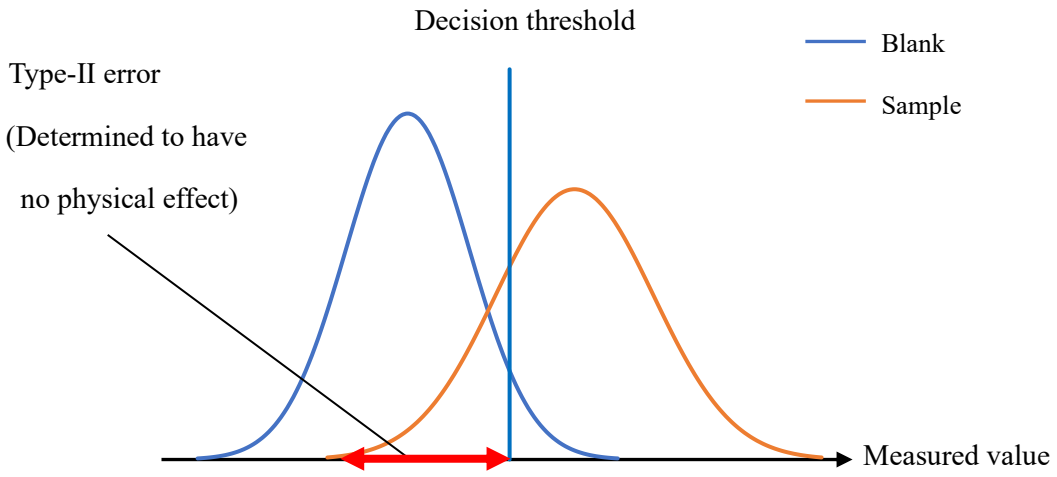
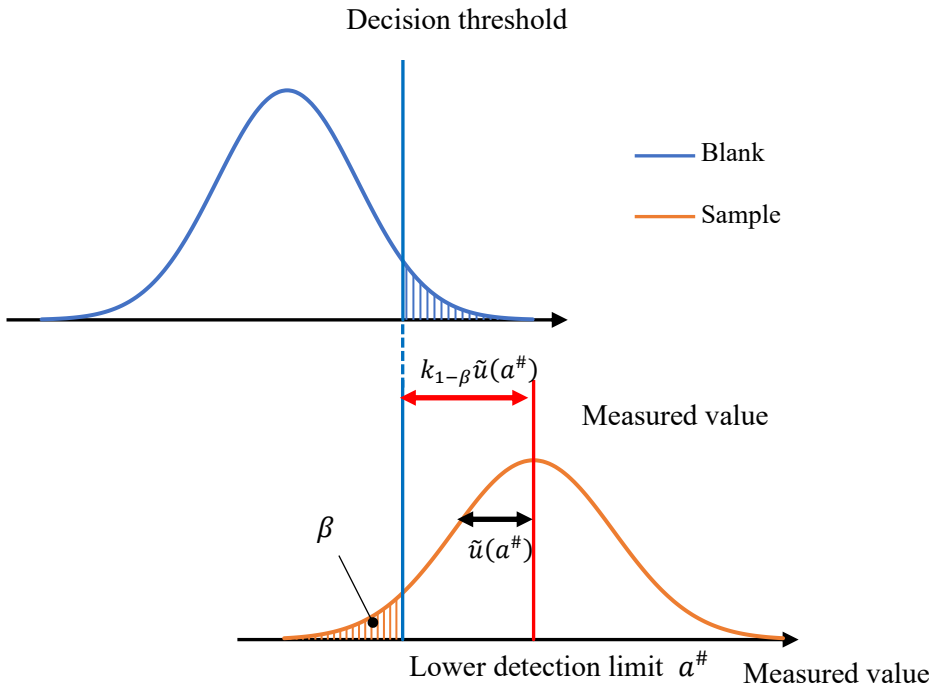


Figure H. 2 Distribution of measured values when the best estimate of the measured quantity is close to the decision threshold

At this time, measured values in the red interval in Figure H. 2 are below the decision threshold, and it is determined that no physical effects exist. Thus, an interval where the confidence level $1-\beta$(risk rate β) is established in the distribution of sample measurements, and the best estimate of the measured quantity when the lower limit of the interval coincides with the decision threshold, as shown in Figure H. 3, is assumed to be the lower detection limit. In this case, the probability of the type-II error is β.



$\tilde{u}(a^{\#})$: uncertainty of the measured quantity when the best estimate is $a^{\#}$

$k_{1-\beta}$: coverage factor for the confidence level of $1-\beta$

Figure H. 3 Lower detection limit

The lower detection limit is used to evaluate the measurement procedure by comparison with the guideline value a_r. When $a^{\#} < a_r$, the measurement procedure is considered as adequate. If $a^{\#} > a_r$, the lower detection limit should be reduced by increasing the measurement time, reviewing the number of counts, etc. ISO 11929-4:2022 sets the guideline value a_r at 3 Bq for general measurements. (For low background counts, the guideline value is 0.1 Bq.)

In this context, the guideline value a_r according to ISO 11929-1:2019 is a value that corresponds to a scientific, legal, or other requirement regarding detection capability and is

intended for the further evaluation of the measurement procedure by comparison with the lower detection limit.

Note 1 As an example, guideline values are given as the radioactivity, specific radioactivity, radioactivity concentration, radioactivity areal density, or dose rate.

Note 2 By comparing the lower detection limit with the guideline value, it is possible to determine whether the measurement procedure meets the requirements set by the guideline value and is therefore suitable for the measurement purpose. The measurement procedure meets the requirement if the detection limit is less than the guideline value.

Note 3 Guideline values should not be mixed with other values specified in conformity requirements or regulatory limits.

Figure H. 4 summarizes the concepts of the decision threshold and lower detection limit in a single figure.

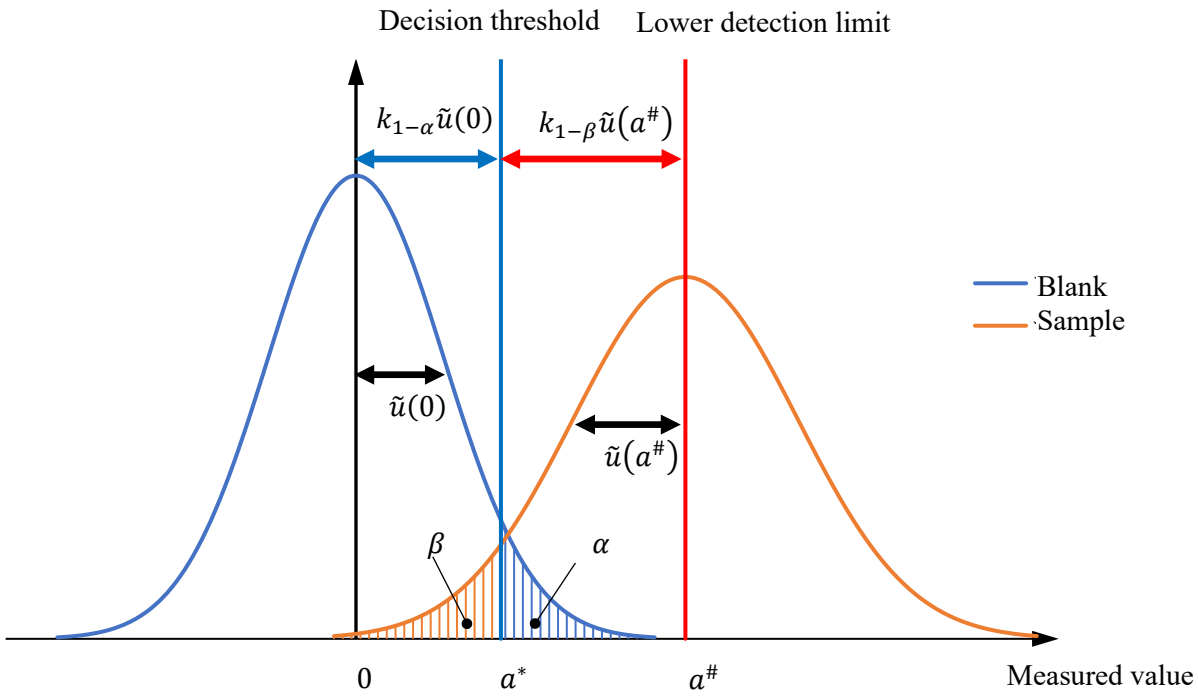


Figure H. 4 Concept of the lower detection limit according to ISO 11929

H.1.4 Example of lower detection limit calculation according to ISO 11929

Derive the decision threshold and lower detection limit using the model equations described in ISO 11929-4[126].

H.1.4.1 General formula for calculating radioactivity from the number of counts

$$a = r_n \cdot w = (r_g - r_0) \cdot w \quad \text{(H.3)}$$

where

a : Measured amount (radioactivity concentration)

r_n : Net counting rate

r_g : Counting rate of sample measurement. When the count of the sample measurement is n_g and measurement time is t_g, $r_g = n_g/t_g$.

r_0 : Counting rate of background measurements. When the count of background measurements is n_0 and the measurement time is t_0, $r_0 = n_0/t_0$.

w : Conversion factor from the counting rate to radioactivity

$$w = \frac{1}{\varepsilon_E \cdot m \cdot D}$$

ε_E : Detection efficiency

m : Sample amount (kg, L, etc.)

However, this is not necessary if a is obtained as radioactivity

D : Decay correction factor

In this case, if the uncertainties of r_n and w are $u(r_n)$ and $u(w)$, respectively, the uncertainty of a in $u(a)$ is expressed as follows:

$$u(a) = r_n \cdot w \cdot \sqrt{\left(\frac{u(r_n)}{r_n}\right)^2 + \left(\frac{u(w)}{w}\right)^2} \quad \text{(H.4)}$$

$$= \sqrt{w^2 u^2(r_n) + r_n^2\, u^2(w)} \quad \text{(H.5)}$$

Furthermore, as $r_n = a/w$ and $u(r_n) = \sqrt{r_g/t_g + r_0/t_0}$ from (H.3), substitute them into (H.5).

[126] ISO 11929-4:2022. Determination of the characteristic limits (decision threshold, detection limit, and limits of the coverage interval) for the measurements of ionizing radiation - Fundamentals and application - Part 4: Guidelines to applications. ISO 11929-4:2022 (2022)

$$u(a) = \sqrt{w^2\left(\frac{r_g}{t_g}+\frac{r_0}{t_0}\right)+a^2\frac{u^2(w)}{w^2}} \quad \text{(H.6)}$$

$u^2(w)/w^2$ represents the relative standard uncertainty $u_{rel}(w)$, excluding the counting uncertainty of measurement.

To calculate the decision threshold and lower detection limit according to ISO 11929, a function of the uncertainty of the measured quantity $\tilde{u}(\tilde{a})$ with the best estimate of the measured quantity $\tilde{a}$ as a variable is needed. From (H.3), the following equation can be expressed using the best estimate $\tilde{a}$:

$$r_g = \frac{\tilde{a}}{w} + r_0 \quad \text{(H.7)}$$

Substituting this into (H.6),

$$\tilde{u}(\tilde{a}) = \sqrt{w^2\left(\left(\frac{\tilde{a}}{w}+r_0\right)/t_g+\frac{r_0}{t_0}\right)+\tilde{a}^2\frac{u^2(w)}{w^2}} \quad \text{(H.8)}$$

is obtained.

H.1.4.2 Decision threshold

Substitute the best estimate of the measured quantity $\tilde{a}=0$ into Equation (H.8) and then into $\tilde{u}(0)$ in Equation (H.1)

$$a^* = k_{1-\alpha}\cdot w\cdot\sqrt{\frac{n_0}{t_0 t_g}+\frac{n_0}{t_0^2}} \quad \text{(H.9)}$$

where

a^* : Decision threshold (Bq or Bq/kg, Bq/L, etc.)

$k_{1-\alpha}$: Coverage factor for the confidence interval that avoids type-I errors (error of detecting something that doesn't exist).

H.1.4.3 Lower detection limit

Assuming that the lower detection limit is $a^{\#}$, substitute $a^{\#}$ into Equation (H.8) and then into $\tilde{u}(a^{\#})$ in Equation (H.2).

$$a^{\#} = a^* + k_{1-\beta}\sqrt{w^2\left(\left(\frac{a^{\#}}{w}+r_0\right)/t_g+\frac{r_0}{t_0}\right)+a^{\#2}\frac{u^2(w)}{w^2}}$$

$$(a^{\#} - a^{*})^2 = k_{1-\beta}^2 \left[w^2 \left(\left(\frac{a^{\#}}{w} + r_0 \right) / t_g + \frac{r_0}{t_0} \right) + a^{\#2} \frac{u^2(w)}{w^2} \right]$$

$$\left(1 - k_{1-\beta}^2 \cdot u_{rel}^2(w)\right) a^{\#2} - 2a^{*}a^{\#} + a^{*2} = k_{1-\beta}^2 w^2 \left(\frac{a^{\#}}{w t_g} + \frac{r_0}{t_g} + \frac{r_0}{t_0} \right) \qquad \text{(H.10)}$$

where when $k_{1-\alpha} = k_{1-\beta} = k$, from Equation (H.9),

$$a^{*2} = k \cdot w \left(\frac{r_0}{t_g} + \frac{r_0}{t_0} \right)$$

therefore, substitute this equation into Equation (H.10),

$$\left(1 - k^2 \cdot u_{rel}^2(w)\right) a^{\#2} - 2a^{*}a^{\#} + a^{*2} = \frac{k^2 w}{t_g} a^{\#} + a^{*2}$$

$$\left(1 - k^2 \cdot u_{rel}^2(w)\right) a^{\#2} - \left(2a^{*} + \frac{k^2 w}{t_g} \right) a^{\#} = 0$$

Solving the following quadratic equation yields the lower detection limit:

$$a^{\#} = \frac{2 \cdot a^{*} + (k^2 \cdot w)/t_g}{1 - k^2 \cdot u_{rel}^2(w)} \qquad \text{(H.11)}$$

where

$a^{\#}$: Lower detection limit (Bq or Bq/kg, Bq/L, etc.)

k : Coverage factor

$k = k_{1-\alpha} = k_{1-\beta}$

$k_{1-\beta}$ Coverage factor for the confidence interval that avoids type-II errors (error of not detecting something that exists).

Generally, the risk rate $\alpha = \beta = 0.05$ (5 %) (coverage factor $k_{1-\alpha} = k_{1-\beta} \fallingdotseq 1.645$).

$u_{rel}(w)$ The relative standard uncertainty of the conversion factor w

The relative standard uncertainty is the combination of all uncertainties related to the respective measurement, excluding uncertainty related to counting in sample measurements.

H.2 Lower detection limit using the Kaiser method

In the measurement, when a sample contains no radionuclides of interest, the net background counts are distributed as shown in Figure H.6. In this case, if the net count value is r_n and statistical uncertainty of counting is σ, the lower detection limit is defined as the detectable limit count value $r_{DL} = k\sigma$.

$$r_{DL} = k\sigma \tag{H.12}$$

where

σ : Uncertainty of counting

k : Coverage factor (often set to 3)

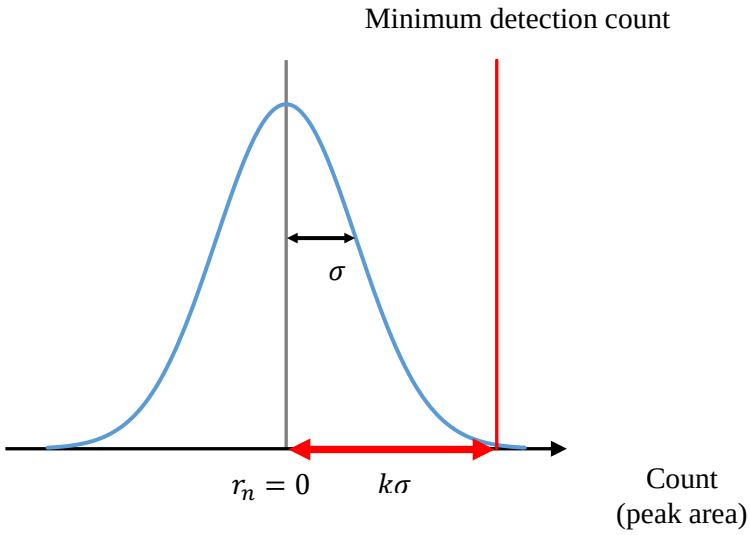


Figure H.6 Schematic of the lower detection limit according to the Kaiser method

Initially, define the following:

r_g : Total counting rate of the sample [cps]

r_0 : Background counting rate [cps]

t_g : Sample measurement time [sec]

t_0 : Background measurement time [sec]

In this case, r_{DL} and σ are represented by the following equations:

$$r_{DL} = r_g - r_0 \tag{H.13}$$

$$\sigma^2 = \frac{r_g}{t_g} + \frac{r_0}{t_0} \tag{H.14}$$

Substituting Equations (H.13) and (H.14) into Equation (H.12) and solving the quadratic equation for r_{DL} yields the detectable limit count

$$r_{DL} = \frac{\frac{k^2}{t_g} + k\sqrt{(\frac{k}{t_g})^2 + 4r_0(\frac{1}{t_g} + \frac{1}{t_0})}}{2} \tag{H.15}$$

The obtained detectable limit count is converted into radioactivity or radioactivity concentration, and these values are used as lower detection limits.

H.3 Example of lower detection limit calculation

In this case, the lower detection limit obtained using the Kaiser method and ISO 11929 is calculated for each of the following cases: (1) when the counting rate of the sample is high and (2) near background.

(1) When the sample counting rate is high

• Measurement conditions

Analysis sample : Water

Analysis method : Distillation method

Sample volume m : 50 [mL]

Measurement time t_g and t_0 : 50 [min]

Detection efficiency ε_E : 27.79 [%]

Uncertainty associated with weighing $u_{rel}(m)$: 0.0058 [%]

Uncertainty associated with instrument calibration $u_{rel}(cal)$: 2.85 [%]

Uncertainty associated with the measurement of samples $u_{rel}(mea)$ (excluding counting uncertainty associated with the sample measurement and background) : 2.79 [%]

Table H.1 Sample and background counts

No.	BG1 count	Sample count	BG2 count
1	190	65,749	191
2	170	65,606	181
3	163	65,374	171
4	180	65,701	187
5	184	65,316	163
6	206	65,376	164
7	197	65,417	188
8	185	64,994	189
9	178	65,426	183
10	173	66,140	182
Total	1,826	655,099	1,799

The background counting rate r_0 [cpm] and sample counting rate r_g [cpm] are as follows:

$$r_0 = \frac{(1826 + 1799)}{50 \times 10 \times 2} = 3.625$$

$$r_g = \frac{655099}{50 \times 10} = 1310$$

Thus, the net counting rate r_n [cpm] and its uncertainty $u(r_n)$ are as follows:

$$r_n = (r_g - r_0)$$

$$= 1310 - 3.625$$

$$= 1306.375$$

$$u(r_n) = \sqrt{\frac{r_g}{t_g} + \frac{r_0}{t_0}}$$

$$= \sqrt{\frac{1310}{50 \times 10} + \frac{3.625}{50 \times 10 \times 2}}$$

$$= 1.620$$

Next, the conversion factor w, uncertainty $u(w)$, and relative standard uncertainty $u_{rel}(w)$ are obtained.

$$w = \frac{1}{\varepsilon_E \cdot m}$$

$$= \frac{1}{\frac{27.79}{100} \times \frac{50}{1000}}$$

$$= 71.97$$

$$u(w) = w\sqrt{u_{rel}^2(m) + u_{rel}^2(cal) + u_{rel}^2(mea)}$$

$$= 71.97 \times \sqrt{\left(\frac{0.0058}{100}\right)^2 + \left(\frac{2.85}{100}\right)^2 + \left(\frac{2.79}{100}\right)^2}$$

$$= 2.87$$

$$u_{rel}(w) = \frac{u(w)}{w}$$

$$= 0.03988$$

Thus, the radioactivity concentration a and combined standard uncertainty $u(a)$ can be obtained.

$$a = \frac{r_n \times w}{60}$$

$$= \frac{1306.375 \times 71.97}{60}$$

$$= 1567$$

$$u(a) = a \times \sqrt{\left(\frac{u(r_n)}{r_n}\right)^2 + \left(\frac{u(w)}{w}\right)^2}$$

$$= 1567 \times \sqrt{\left(\frac{1.620}{1306.375}\right)^2 + \left(\frac{2.87}{71.97}\right)^2}$$

$$= 62.52$$

Next, the lower detection limit by the Kaiser method is determined. The detectable counting rate r_{DL} [cpm] is obtained using Equation (H.15).

$$r_{DL} = \frac{\frac{k^2}{t_g} + k\sqrt{(\frac{k}{t_g})^2 + 4r_0(\frac{1}{t_g} + \frac{1}{t_0})}}{2}$$

$$= \frac{\frac{3^2}{50 \times 10} + 3\sqrt{(\frac{3}{50 \times 10})^2 + 4 \times 3.625 \times (\frac{1}{50 \times 10} + \frac{1}{50 \times 10 \times 2})}}{2}$$

$$= 0.3220$$

Finally, the counting rate is converted to the radioactivity concentration using the sample amount and counting efficiency, and the lower detection limit $a^{\#}_{Kaiser}$ [Bq/L] is obtained.

$$a^{\#}_{Kaiser} = \frac{r_{DL}}{m \times \varepsilon_E \times 60}$$

$$= \frac{0.3220}{\frac{50}{1000} \times \frac{27.79}{100} \times 60}$$

$$= 0.3862$$

Meanwhile, the lower detection limit according to ISO 11929 $a^{\#}_{ISO11929}$ is obtained from Equations (H.9) and (H.11), together with the decision threshold.

$$a^* = k_{1-\alpha} \cdot w \cdot \sqrt{\frac{n_0}{t_0 t_g} + \frac{n_0}{t_0^2}}$$

$$= 1.645 \cdot 71.97$$

$$\cdot \sqrt{\frac{1826 + 1799}{(50 \times 10 \times 2 \times 60) \times (50 \times 10 \times 60)} + \frac{1826 + 1799}{(50 \times 10 \times 2 \times 60) \times (50 \times 10 \times 2 \times 60)}}$$

$= 0.2058$

$$a^{\#}_{ISO11929} = \frac{2 \cdot a^{*} + \frac{k^2 \cdot w}{t_g}}{1 - k^2 \cdot u^2_{rel}(w)}$$

$$= \frac{2 \cdot 0.2058 + \frac{1.645^2 \cdot 71.97}{50 \times 10 \times 60}}{1 - 1.645^2 \cdot 0.03988^2}$$

$$= 0.4199$$

These results are summarized in Table H.2. For the ease of calculation, no half life correction was performed in sample measurements.

Table H.2 Lower detection limits for each parameter and each calculation method

Parameter	Kaiser method	ISO 11929
Radioactivity concentration a [Bq/L]	1,567	
Combined standard uncertainty $u(a)$ [Bq/L]	62.52	
Decision threshold a^{*} [Bq/L]		0.2058
Lower detection limit $a^{\#}$ [Bq/L]	0.3862	0.4199
Ratio to Kaiser [%]		8.0

(2) When the sample counting rate is near background

○ Measurement conditions

Analysis sample : Water

Analysis method : Distillation method

Sample volume m : 50 [mL]

Measurement time t_g and t_0 : 50 [min]

Detection efficiency ε_E : 28.61 [%]

Uncertainty associated with weighing $u_{rel}(m)$: 0.0127 [%]

Uncertainty associated with instrument calibration $u_{rel}(cal)$: 2.60 [%]

Uncertainty associated with the measurement of samples $u_{rel}(mea)$ (excluding sample measurement and counting uncertainty associated with background): 2.88 [%]

Table H.3 Sample and background counts

No.	BG1 count	Sample count	BG2 count
1	127	125	122
2	112	145	109
3	134	148	130
4	123	146	144
5	148	149	137
6	138	134	137
7	124	136	118
8	138	143	145
9	125	142	103
10	125	125	133
Total	1,294	1,393	1,278

The background counting rate r_0 [cpm] and sample counting rate r_g [cpm] are as follows:

$$r_0 = \frac{(1294 + 1278)}{50 \times 10 \times 2} = 2.572$$

$$r_g = \frac{1393}{50 \times 10} = 2.786$$

Thus, the net counting rate r_n [cpm] and its uncertainty $u(r_n)$ are:

$$r_n = (r_g - r_0) = 2.572 - 2.786 = 0.214$$

$$u(r_n) = \sqrt{\frac{r_g}{t_g} + \frac{r_0}{t_0}}$$

$$= \sqrt{\frac{2.786}{50 \times 10} + \frac{2.572}{50 \times 10 \times 2}}$$

$$= 0.09024$$

Next, the conversion factor w, uncertainty $u(w)$, and relative standard uncertainty $u_{rel}(w)$ are obtained.

$$w = \frac{1}{\varepsilon_E \cdot m}$$

$$w = \frac{1}{\frac{28.61}{100} \times \frac{50}{1000}} = 69.91$$

$$u(w) = w\sqrt{u_{rel}^2(m) + u_{rel}^2(cal) + u_{rel}^2(mea)}$$

$$= 69.91 \times \sqrt{\left(\frac{0.0127}{100}\right)^2 + \left(\frac{2.60}{100}\right)^2 + \left(\frac{2.88}{100}\right)^2}$$

$$= 2.71$$

$$u_{rel}(w) = \frac{u(w)}{w}$$

$$= 0.03876$$

Thus, we can obtain the radioactivity concentration a and combined standard uncertainty $u(a)$.

$$a = \frac{r_n \times w}{60}$$

$$= \frac{0.214 \times 69.91}{60}$$

$$= 0.2493$$

$$u(a) = A \times \sqrt{\left(\frac{u(r_n)}{r_n}\right)^2 + \left(\frac{u(w)}{w}\right)^2}$$

$$= 0.2493 \times \sqrt{\left(\frac{0.09024}{0.214}\right)^2 + \left(\frac{2.71}{69.91}\right)^2}$$

$$= 0.1056$$

Next, the lower detection limit by the Kaiser method is determined. The detectable counting rate r_{DL} [cpm] is obtained using Equation (H.15).

$$r_{DL} = \frac{\frac{k^2}{t_g} + k\sqrt{(\frac{k}{t_g})^2 + 4r_0(\frac{1}{t_g} + \frac{1}{t_0})}}{2}$$

$$= \frac{\frac{3^2}{50 \times 10} + 3\sqrt{(\frac{3}{50 \times 10})^2 + 4 \times 2.572 \times (\frac{1}{50 \times 10} + \frac{1}{50 \times 10 \times 2})}}{2}$$

$$= 0.2727$$

Finally, the counting rate is converted to the radioactivity concentration using the sample amount, counting efficiency, etc., and the lower detection limit $a^{\#}_{Kaiser}$ is obtained.

$$a^{\#}_{Kaiser} = \frac{r_{DL}}{m \times \varepsilon_E \times 60}$$

$$= \frac{0.2727}{\frac{50}{1000} \times \frac{28.61}{100} \times 60}$$

$$= 0.3177$$

Meanwhile, the lower detection limit according to ISO 11929 $a^{\#}_{ISO11929}$is obtained from Equations (H.9) and (H.11), together with the decision threshold.

$$a^{*} = k_{1-\alpha} \cdot w \cdot \sqrt{\frac{n_0}{t_0 t_g} + \frac{n_0}{t_0^2}}$$

$$= 1.645 \cdot 69.91$$

$$\cdot \sqrt{\frac{1294 + 1278}{(50 \times 10 \times 2 \times 60) \times (50 \times 10 \times 60)} + \frac{1294 + 1278}{(50 \times 10 \times 2 \times 60) \times (50 \times 10 \times 2 \times 60)}}$$

$$= 0.1684$$

$$a^{\#}_{ISO11929} = \frac{2 \cdot a^{*} + \frac{k^2 \cdot w}{t_g}}{1 - k^2 \cdot u^2_{rel}(w)}$$

$$= \frac{2 \cdot 0.1684 + \frac{1.645^2 \cdot 69.91}{50 \times 10 \times 60}}{1 - 1.645^2 \cdot 0.03876^2}$$

$$= 0.3445$$

The results are summarized in Table H.4. For the ease of calculation, no half life correction was performed in sample measurements.

Table H.4 Lower detection limits for each parameter and each calculation method

Parameter	Kaiser method	ISO11929
Radioactivity concentration a [Bq/L]	0.2493	
Combined standard uncertainty $u(a)$ [Bq/L]	0.1056	
Decision threshold a^{*} [Bq/L]		0.1683
Lower detection limit $a^{\#}$ [Bq/L]	0.3177	0.3445
Ratio to Kaiser [%]		7.8

In this case, the results remain nondetectable for the Kaiser method and ISO 11929.

Information

Information A Study of purification method for water samples using ion-exchange resins

(1) Objective

The method for removing impurities from water samples using ion-exchange resins (a mixture of anion- and cation-exchange resins) does not require glassware or electrical equipment employed in the distillation method and can be performed in a short time. Therefore, it is an effective alternative to distillation in situations where a large number of samples must be prepared in an emergency or where the rapid reporting of results is required. This method is suitable for samples with low salinity, such as tap water, river water, and rainwater, but unsuitable for samples with high salinity, including seawater, because residual ions may not be removed completely or the column may become clogged. Thus, whether diluted seawater samples can be purified using this method was examined.

(2) Method

1) Anion- and cation-exchange resins (particle size >60 mesh, max. 5%) conditioned with ion-exchange water (add ion-exchange water to ion-exchange resins in a beaker, stir, decant, and repeat the same operation once again) were mixed in a 1:1 ratio, and 15 mL of this resin was packed into a polyethylene column.
2) A tritium standard solution is added to tap water and seawater (undiluted, diluted 20 times, and diluted 100 times) to prepare 100 Bq/L water samples.
3) A total of 90 mL of each water sample was passed through the ion-exchange resin column, and the elute was fractioned into 15 mL portions.
4) The electrical conductivity (mS/m) and radioactivity concentration of each portion (15 mL) were measured.

(3) Results

The results of the electrical conductivity measurements are shown in Table A.1. With the raw seawater solution, resins contracted immediately after introducing the sample, causing air bubbles to form inside the column. The initial fractions (0–15 mL) had an electrical conductivity of less than 1 mS/m. However, in next fractions (15–30 mL), electrical conductivity increased considerably and was considered to exceed the ion-removal capacity of resins. Furthermore, the next fractions (30–45 mL) completely clogged the column and stopped the liquid flow

completely. Based on the above observations, it was confirmed that this method is not suitable for the purification of raw seawater solutions. For all elutes except for the raw seawater solution, electrical conductivity was 0 or 1 mS/m or less, confirming that dissolved ions in water samples were sufficiently removed. However, for the sample in which seawater was diluted 20 times, bubbles were generated when using the 75–90 mL fraction, and electrical conductivity was higher than that in other fractions. Therefore, it is recommended to limit the maximum volume of a sample containing seawater diluted 20 times to approximately 90 mL (six times the resin volume). The results of radioactivity concentration measurements are shown in Table A.2. The radioactivity concentration of the initial fraction (015 mL) was approximately 7%–19% the concentration of the sample water (100 Bq/L), and the composition of the elute was more than 80% water originally contained in the column. It is considered necessary to take out the measurement sample after flowing at least twice the volume of water sample (30 mL) as the resin volume (15 mL). Based on the above, the analysis flow is depicted in Figure A.1. Using seawater diluted 20 times, it is possible to purify a sample (60 mL) that is approximately four times the amount of resin (15 mL). If a 100-mL vial is used and measurements are performed for 100 min, the detectable level is expected to be ~20 Bq/L, as shown in Appendix Table A.3.

Table A.1 Electrical conductivity measurement results. Unit: mS/m

Fraction	Tap water	Seawater (100x dilution)	Seawater (20x dilution)	Seawater (Undiluted)
Before purification	23	64	280	4,400
0–15 mL	0.0	0.0	0.0	0.3
15–30 mL	0.0	0.0	0.0	6,700
30–45 mL	0.0	0.0	0.0	Column clogged
45–60 mL	0.0	0.0	0.0	Column clogged
60–75 mL	0.0	0.0	0.0	Column clogged
75–90 mL	0.0	0.0	0.4	Column clogged

Table A.2 Results of radioactivity concentration measurements. Unit: Bq/L

Fraction	Tap water	Seawater (100x dilution)	Seawater (20x dilution)
0–15 mL	7.3 ± 3.7	19.0 ± 3.7	11.9 ± 3.2
15–30 mL	104 ± 4.5	97.8 ± 4.4	97.2 ± 3.8
30–45 mL	97.4 ± 4.4	108 ± 4.5	102 ± 3.9
45–60 mL	104 ± 4.5	106 ± 4.4	105 ± 3.9
60–75 mL	101 ± 4.5	112 ± 4.5	107 ± 3.9
75–90 mL	97.7 ± 4.5	98.6 ± 4.4	99.6 ± 3.8

In the table, " $\pm$ " represents the standard uncertainty ($k = 1$) associated with counting.

Table A.3 Detectable levels of tritium in seawater samples (purified using ion-exchange resin)

Measurement container	Measurement time (min)	Detectable level (Bq/L) *1 – *3	
		Seawater (diluted 20 times)	Diluted 100 times
20-mL glass vial	100	200	1000
	500	100	500
	1000	60	300
100-mL fluoroplastic vial	100	20	100
	500	10	50
	1000	6	30

*1 The mixing ratio of the water sample and emulsified scintillator shall be 1:1.

*2 The counting efficiency of the liquid scintillation counter (LSC) shall be 25%.

*3 The background counting rate for each container is 20 cpm for a 20-mL glass vial and 4 cpm for a 100-mL fluoroplastic vial.

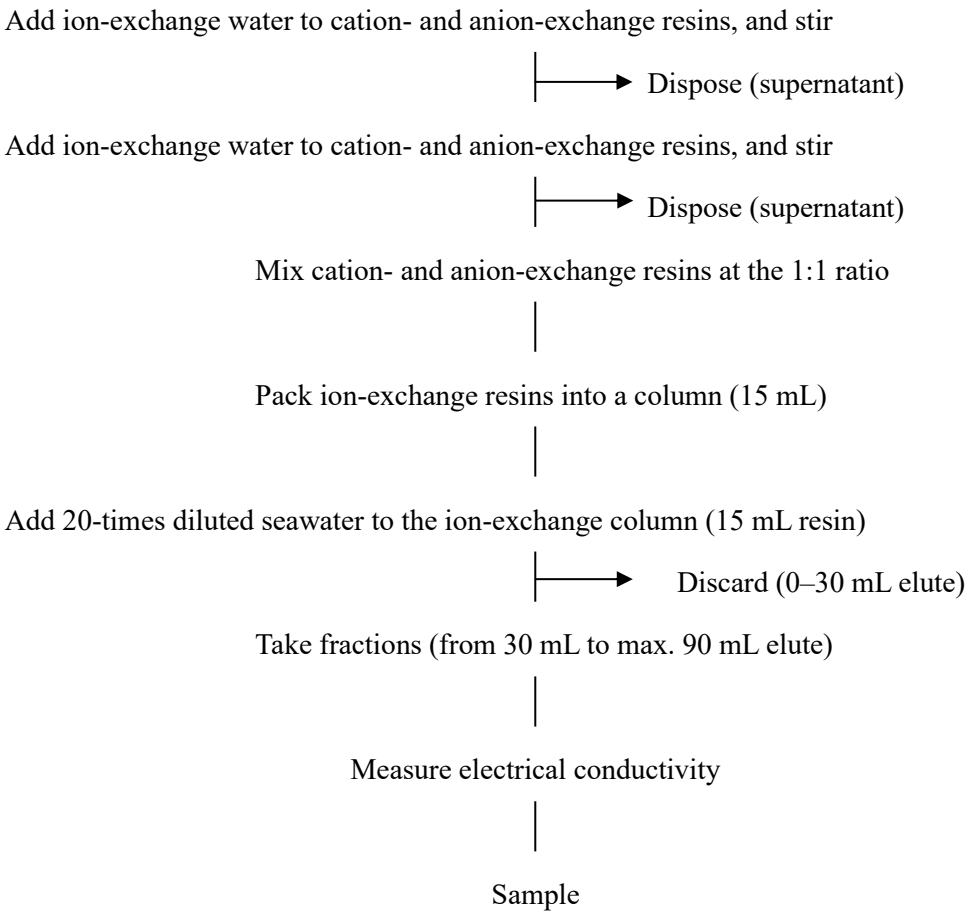


Figure A.1 Analysis flow

Information B Collecting tritium from the atmosphere using bubbling and condensation methods

This section introduces the bubbling and moisture condensation methods, which have been used by analytical laboratories outside Japan as methods for collecting tritium in air, other than the molecular sieve method, silica-gel method, dehumidifier method, and passive method.

B.1 Bubbling method[127]

In the bubbling method, air passes through a trap solution in a vial, and HTO, catalyst-oxidized HT, and organic tritium (e.g., CH_3T) are collected by bubbling. This section introduces the apparatus[128] used by the Vietnam Atomic Energy Research Institute to survey areas around nuclear power plants. An overview of the apparatus is shown below, and a schematic of the apparatus is shown in Figure B.1.

[Overview]

1) Air drawn in by a pump (7 in the figure) passes through a filter (1 in the figure), where airborne dust and other particulate matter are removed.
2) Filtered air then passes through a flowmeter (2 in the figure), which displays the current flow rate and integrated flow rate
3) Air passing through the flowmeter is bubbled into a trap solution* (tritium-free water or water with a known tritium concentration) in the unit (3 in the figure) in which two vials are connected in series, and HTO is collected in the trap solution[129].

   *Cooled with an antifreeze at 7°C–15°C to prevent evaporation (4 in the figure)
4) After collecting HTO, air is introduced into a platinum-alumina catalyst column (5 in the figure) heated in an electric furnace (450°C–500°C), where HT and organic tritium (e.g., CH_3T) are oxidized into HTO[130].
5) Air passed through the catalyst column is bubbled into the trap solution in the unit (6 in the figure) in which two vials are connected in series, and HT and organic tritium (such as CH_3T) are collected as HTO.

---

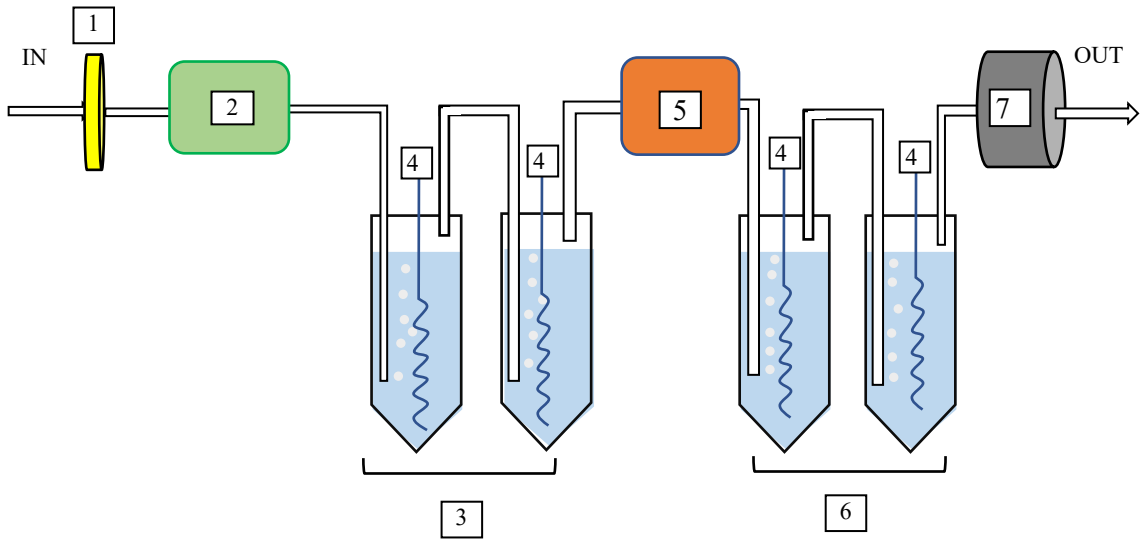
[127] V. Thu Bac et al., Study to Build up Method for Determining Radioactivity of h-3 in Atmosphere, *Annual Report for 2014 (VINATOM-AR 14-11)*, 109-117 (2015).

[128] ISO 20041-1:2022, Tritium and carbon-14 activity in gaseous effluents and gas discharges of nuclear installations - Part 1: Sampling of tritium and carbon-14. ISO 20041-1:2022(2022)

[129] The collection efficiency is 99% ± 7% (manufacturer's catalog value).

[130] The furnace efficiency (HT => HTO) is 98% ± 11% (manufacturer's catalog value).

Note that at least 160 mL trap solution needs to be added, and if more than 180 mL is added, it will exceed the capacity of the vial and flow into the next vial. Therefore, the amount of water that can be collected is limited to 20 mL per vial, and as it is diluted by a factor of more than nine, electrolysis enrichment is required for environmental samples with low tritium concentrations. In addition, because there is no function to monitor the amount of water in the vial or alert the user, the water volume must be monitored visually on a regular basis. The amount of water collected is measured using a mass method and used together with the integrated flow rate, temperature, and humidity to calculate the tritium concentration in air.



1. Filter 2. Flowmeter 3. Vials (for HTO collection) 4. Cooling unit
5. Oven (+ catalyst column) 6. Vials (for HT collection) 7. Pump

Figure B.1 Schematic of the atmospheric-tritium-collection system using the bubbling method

B.2 Condensation method[131]

The condensation method is used to collect HTO by cooling and condensing water vapor in the atmosphere under pressure. This document shows an example of the apparatus used to measure the tritium concentration in exhaust gas at the Tokai Reprocessing Plant, the Japan Atomic Energy Agency (JAEA). For more information on the details and performance of this device, refer to the report by Koarashi et al.[132]. The flow of water collection by the apparatus and a schematic of the apparatus are shown in Figure B.2.

[Overview]

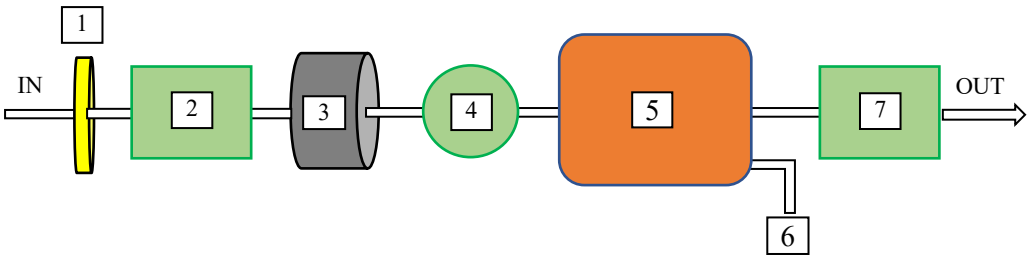
1) Air drawn in by a pump (3 in the figure) passes through a filter (1 in the figure), where airborne dust and other particulate matter are removed.
2) Air that passed through the filter is introduced into a pressure gauge (4 in the figure) and a moisture collector (5 in the figure), where it is cooled to −32°C under pressure (approximately 2.2 atm)[133] to condense HTO in the moisture collector.
3) After HTO collection, air passes through the flowmeter (7 in the figure), which displays the current flow rate and integrated flow rate.
4) After completing collection, the condensed moisture is heated, dissolved, and collected from the moisture collection port (6 in the figure).

When continuous collection is performed for one week at a flow rate of 0.4 L/min in the summer when there is a high water content in air, collection efficiency is over 98%, and approximately 60–80 g water can be collected. The detectable level is comparable to the method using molecular sieves. The amount of water collected is measured using a mass method and used together with the integrated flow rate, temperature, and humidity to calculate the tritium concentration in air.

[131] ISO 20041-1:2022, Tritium and carbon-14 activity in gaseous effluents and gas discharges of nuclear installations - Part 1: Sampling of tritium and carbon-14. ISO 20041-1:2022(2022).

[132] 小嵐淳ら : 排気中トリチウムモニタリング手法の検証（再評価）と高度化への提言,核燃料サイクル開発機構 東海事業所　技術報告（JNC TN8410 2005-004）(2005).

[133] When the temperature of the moisture collector is −32°C, collection efficiency falls below 90% under atmospheric pressure; however, by increasing the pressure of the moisture collector to 1.5 atm or higher, a collection efficiency of 90% or higher can be achieved. When the temperature of the moisture collector is −25°C, a collection efficiency of 90% or more can be obtained by setting the pressure of the moisture collector to 2.0 atm or higher.



1. Filter 2. Thermo-hygrometer 3. Pump 4. Pressure gauge 5. Moisture collector 6. Moisture collection port 7. Flowmeter

Figure B.2 Schematic of the atmospheric-tritium-collection system using the condensation method

Information C Analysis procedure for nonexchangeable OBT

This section describes a procedure for separating tritium into TFWT and OBT via vacuum freeze drying for the tritium analysis of biological samples. Tritium in OBT can be divided into exchangeable OBT (OBT that bonds to oxygen and nitrogen atoms and readily exchanges with TFWT) and nonexchangeable OBT (OBT that bonds to a carbon chain and does not readily exchange with TFWT). Compared with TFWT and exchangeable OBT, nonexchangeable OBT takes longer to be excreted from biological tissues and is stored in tissues for a longer period of time. Many studies have investigated nonexchangeable OBT because it is considered important for accurate dose assessment. In addition, "tritiated organic compounds" produced by the medical, pharmaceutical, and chemical industries as radiopharmaceuticals, when released directly into the environment, may be effectively absorbed into organisms in the ecosystem, resulting in a considerable increase in the OBT concentrations. Therefore, nonexchangeable OBT analysis is essential for monitoring purposes.

Furthermore, considering that the analysis of nonexchangeable OBT requires a more complicated procedure and that the quantification of OBT without removing exchangeable OBT is sufficient for monitoring results as tritium is unlikely to be concentrated in biological samples, the analytical procedure for nonexchangeable OBT is presented here for reference alone.

C.1 Removal of exchangeable OBT

Exchangeable OBT is removed by the isotope exchange of hydrogen and tritium using tritium-free water[134]. The sample for OBT removal after vacuum freeze drying is immersed in tritium-free water at a volume equal to or greater than TFWT. After the transfer of exchangeable OBT to water through isotope exchange (it is left for a certain period to promote isotope exchange), it is frozen while immersed in tritium-free water. The frozen sample is again subjected to the vacuum freeze-drying process to separate it into water (ice) and dry matter to remove any exchangeable OBT that has migrated into water. To sufficiently remove exchangeable OBT, washing with tritium-free water is performed multiple times.

C.2 Number of washings with tritium-free water

[134] For washing, hot spring water or others in which tritium has not been detected through electrolytic enrichment methods can be used.

The number of washing with tritium-free water was studied by Tamari et al[135]. using dried grass collected from France. Deep well water, which has been confirmed to be tritium-free via electrolytic enrichment, was used to remove exchangeable OBT. A total of 250 mL tritium-free water was added to 30 g dried grass, soaked for 24 h, and dried at 60°C[136]. To ensure the removal of exchangeable OBT, this washing procedure was repeated three times.

To estimate the amount of exchangeable OBT removed, washing solutions were collected and tritium contained in each washing solution was measured. The results for the exchangeable OBT concentration in each washing solution are shown in Table C.1. In the table, " ± " represents the standard uncertainty ($k = 1$) associated with counting.

Table C.1 Tritium removed from the sample via washing[135]

Washing times	Tritium activity (Bq/kg dry matter)
1	4.1 ± 0.7
2	4.7 ± 0.7
3	<2.0
Total	8.9 ± 0.9

Table C.1 indicates that the tritium concentration in the washing solution obtained after the third washing was below the lower detection limit (<2.0 Bq/kg). It was reported that after washing three times with tritium-free water, exchangeable OBT was removed, and tritium contained in the dried sample after washing was nonexchangeable OBT. Additionally, the authors compared radiation measurements performed using an LSC with the mass spectrometry results and reported that the difference in the tritium concentration with and without washing pretreatment obtained via mass spectrometry was in good agreement with the tritium concentration in washing water.

Although quantifying tritium in the washing solution will be a reliable way to confirm whether exchangeable OBT has been removed, this method is complex and increase the number of days required for analysis. Therefore, the appropriateness of washing three times was verified using other dried samples. Verification was performed using dry pine needle samples and hot spring water for washing

[135] T. Tamari et al., OBT Measurement of Vegetation by Mass Spectrometry and Radiometry. Fusion Sci. Technol., 60(4), 1252-1255 (2011).

[136] Although a dryer was used in this paper, it is better to perform the process via vacuum freeze drying as the tritium atmosphere in the dryer may affect the process.

exchangeable OBT, which was confirmed to be tritium-free by electrolytic enrichment. In the analysis, tritium in the dry matter without washing, tritium in each washing solution obtained in three washings, and tritium in the dry matter after washing were evaluated for total OBT, exchangeable OBT, and nonexchangeable OBT, respectively. The results of tritium quantification for each fraction are shown in Table C.2. A comparison of the tritium concentration with and without tritium-free water washing is shown in Figure C.1.

Table C.2 Results of tritium quantification for each fraction

Fraction	Tritium radioactivity (Bq)	Remarks
Washing solution (first time)	1.10 ± 0.048	Exchangeable tritium (A)
Washing solution (second time)	0.16 ± 0.038	
Washing solution (third time)	<Lower detection limit	
Dry matter after washing	1.99 ± 0.013	Nonexchangeable tritium (B)
Unwashed dry matter	3.08 ± 0.017	Total OBT (C)
[(A) + (B)]/(C)	1.05 ± 0.021	—

In the table, " ± " represents the standard uncertainty ($k = 1$) associated with counting.

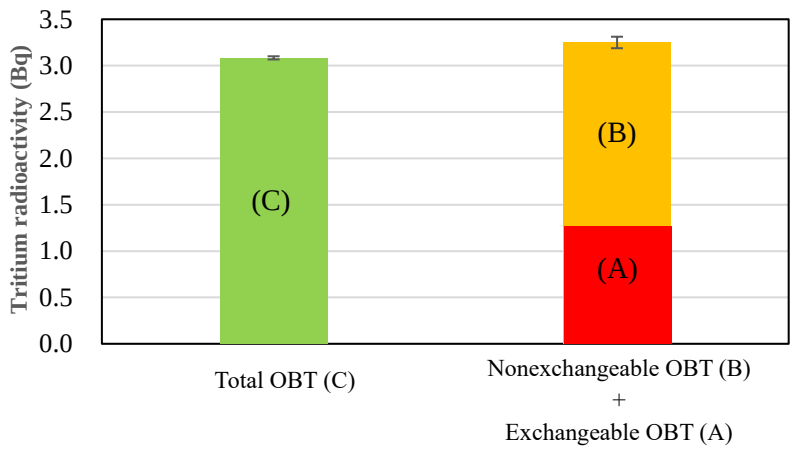


Figure C.1 Comparison of the tritium concentration with and without washings with tritium-free water

According to Table C.2, when the number of washings was verified using dried pine needles, tritium in washing water reduced to below the detection limit after washing three times. In addition, regarding the tritium concentration, the sum of exchangeable OBT (Bq) in washing solutions and nonexchangeable OBT (Bq) in dried matter after washing was in good agreement with the total OBT (Bq) without washing,

and no operational tritium loss was observed. As shown in Table C.3, the same verification was performed thrice, and the tritium concentration was in good agreement with all results.

Table C.3 Tritium concentration with and without washing with tritium-free water

	Tritium concentration ratio*
First verification	1.05 ± 0.021
Second verification	1.05 ± 0.018
Third verification	1.04 ± 0.018

*Tritium concentration ratio = (exchangeable OBT + nonexchangeable OBT)/total OBT

C.3 Analysis flow of nonexchangeable OBT

Based on the existing reports and verification results on the number of washings shown in C.2, it is considered that exchangeable OBT can be sufficiently removed by three washings with tritium-free water. Based on this observation, the analysis flow for nonexchangeable OBT is displayed in Figure C.2.

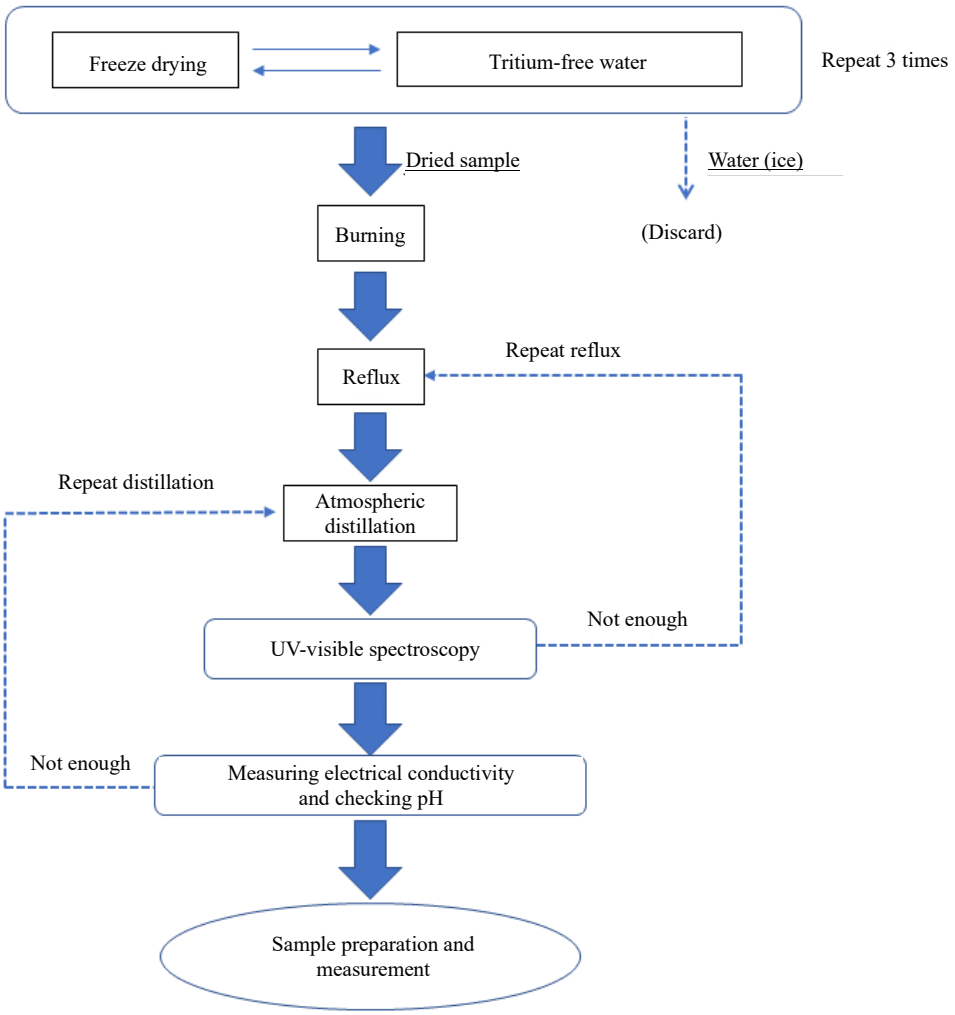


Figure C.2: Analysis flow of nonexchangeable OBT

C.4 Cross check

Nonexchangeable OBT in brewer's rice was analyzed at each laboratory according to the analytical flow depicted in C.3.

(1) Sample preparation

Brewer’s rice was vacuum freeze dried, and the dried material (85.9% dry residue) was thoroughly mixed and then sealed in an aluminum-coated bag to be used as the analysis sample. In addition, a homogeneity test was performed using an elemental analysis with fluorescent X-rays (n = 6, an average value of five measurements). The results of the homogeneity test are shown in Table C.4. The coefficient of variation for each element was at most 2%.

Table C.4 Results of the homogeneity test of analyzed samples Unit: weight percentage

	Mg	P	S	K	Ca
Brewer’s rice 1	0.118	0.217	0.104	0.100	0.0066
Brewer’s rice 2	0.122	0.218	0.105	0.0098	0.0064
Brewer’s rice 3	0.122	0.225	0.108	0.100	0.0066
Brewer’s rice 4	0.118	0.218	0.108	0.101	0.0067
Brewer’s rice 5	0.121	0.221	0.104	0.100	0.0065
Brewer’s rice 6	0.121	0.221	0.107	0.099	0.0064
Average	0.120	0.220	0.106	0.0994	0.0065
Standard deviation	0.0018	0.0030	0.0018	0.00098	0.00013
Coefficient of variation [%]	1.5	1.3	1.7	0.98	1.9

(2) Cross-checking institutions

Institutions that conducted cross-checks are listed below.

KAKEN Corporation

Kyushu Environmental Evaluation Association

Japan Chemical Analysis Center

Hirosaki University

(3) Analysis method

[Tritium-exchange operation]

1) After recording the empty weight of the container for freeze drying (hereinafter referred to as the sample container), the sample was divided into sample containers, and the weight of the sample containers was recorded.
2) At least 125 mL tritium-free water (BG water) was added per 100 g sample weight, and the sample was stirred with a glass rod so that the entire sample was incorporated into BG water.
3) After washing away the sample adhering to the glass rod and sample container wall with BG water, the weight of the sample container was recorded.
4) The container was capped and allowed to stand at room temperature for at least 6 h and then frozen in the freezer for at least overnight.
5) The sample was freeze dried until its weight became almost constant*, and the weight of the sample container was recorded.

   * Difference from the weight measured the day before (or last time) is less than 1 g
6) Steps 2) – 5) were repeated two more times (three times in total).
7) The entire sample was suitably crushed and mixed to make an analysis sample for OBT (hereinafter referred to as analysis sample).

[Pretreatment - Measurement]

1) After weighing the required amount of analysis sample and recording the amount of the combustion sample, dry decomposition was performed. Further, the combustion product water was collected, and the amount of collected water was recorded.
2) The wet decomposition (refluxing) of the combustion product water was performed for at least 4 h.

3) After the distillation of the refluxed sample, conductivity and organic residue content were measured (absorbance measurement), and refluxing and redistillation were repeated if necessary.

4) The distilled sample was mixed with a scintillator in any ratio and used as the measurement sample.

5) Samples with a radioactivity concentration of approximately 0.2 Bq/L (or 0.08 Bq/kg of raw mass sample (85.9 % dry residue)) were measured under detectable conditions, and the radioactivity concentration (Bq/L and Bq/kg of raw mass) and uncertainty were calculated.

(4) Results

The results of cross check are shown in Table C.5. The measurement results were evaluated for E_n score[137] using the measurement results from the Japan Chemical Analysis Center as the standard value. All E_n scores for each institution were within the criteria ($|E_n| \leq 1$), confirming the validity of this analysis method.

Table C.5 Results of cross check

Unit: Bq/kg of raw mass

Sample name / Analysis institution	Nonexchangeable OBT in brewer's rice	E_n score	Remarks
Japan Analysis Center	0.15 ± 0.036	—	Sample volume 50 mL, 2,000 min measurement, Lower detection limit 0.11 Bq/kg of raw mass, unit conversion performed using the hydrogen content
A	0.11 ± 0.024	−0.39	Sample volume 65 mL, 7,000 min measurement, Lower detection limit 0.09 Bq/kg of raw mass, unit conversion performed using the hydrogen content
B	0.12 ± 0.011	−0.37	Sample volume 50 mL, 2,000 min measurement, Lower detection limit 0.11 Bq/kg of raw mass, unit conversion performed using the hydrogen content
C	0.23 ± 0.034	0.87	Sample volume 50 mL, 2,000 min measurement, Lower detection limit 0.11 Bq/kg of raw mass, unit conversion performed using the hydrogen content
Average	0.15		
Standard deviation	0.054		
Coefficient of variation (%)	36		
Range	0.11–0.23		

In the table, " ± " represents the combined standard uncertainty ($k = 1$).

[137] One method was used to evaluate the skills of a testing laboratory. The following equation is used to express performance, and if the absolute value of the En score is less than 1, performance is considered satisfactory.

$$En = \frac{Analysis\ value_{lab} - Analysis\ value_{ref}}{\sqrt{{U_{lab}}^2 + {U_{ref}}^2}}$$

U_{lab}: expanded uncertainty of participating laboratory (coverage factor k = 2)

U_{ref}: expanded uncertainty of the reference laboratory or assigned value (coverage factor k = 2)

Information D Quantification of tritium via ^{3}He mass spectrometry

Although β-ray measurement using an LSC is commonly used for the quantification of tritium, tritium can be estimated via measuring the mass spectrum of the decay product, ^{3}He. This manual is based on the measurement of tritium β-rays using an LSC; however, mass spectrometry is also introduced here as an alternative method for quantifying tritium. The ^{3}He mass spectrometry method presented in this manual is based on the results of a survey conducted by the Institute for Environmental Sciences. When quantifying tritium via mass spectrometry, the sample is first stored in a sealed container to accumulate ^{3}He produced from tritium (Figure D.1). As the storage period increases, the amount of ^{3}He produced also increases, which is advantageous for measuring very low concentrations of tritium. The sealed container is made of aluminosilicate glass (Schott 8252: see Figure D.2), a material that is impermeable to helium, and airborne He in the container is removed by venting it thoroughly (pressure below 10^{-4} Pa) (by adding acetone to the container and venting together with acetone vapor). To produce ^{3}He, the sealed container is left at −30 °C for approximately two months after venting. Generated ^{3}He is introduced into the gas purification line and measured with a noble-gas mass spectrometer (Figure D.3)[138,139,140]. From the atomic number of ^{3}He (N_{He}) obtained via noble-gas mass spectrometry, the atomic number of tritium in the sample (N_0) can be determined using Equation (D.1), and tritium radioactivity (A_0) (Bq) can be estimated utilizing Equation (D.2)[141].

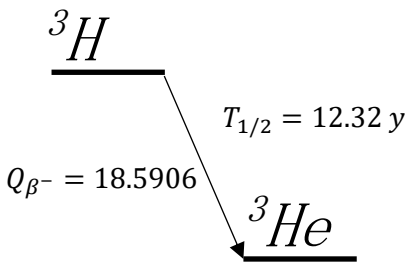


Figure D.1 Tritium-decay mode

$$N_0 = \frac{N_{He}}{(1 - e^{-\lambda \cdot t})} \quad \text{... (D. 1)}$$

$$A_0 = \lambda \cdot N_0 \quad \text{... (D. 2)}$$

where λ is the decay constant of tritium and t is the storage period.

[138] 柿内秀樹, 赤田尚史: 原子力関連施設周辺での環境トリチウムモニタリングの実際, J. Plasma Fusion Res. 89(10), 645-651(2013).

[139] Kakiuchi, H. et al., Low-Level Measurement with a Noble Gas Mass Spectrometer for Organically Bound Tritium in Environmental Samples. *Fusion Sci. Technol.*, **60(4)**, 1256-1259 (2011).

[140] 玉利俊哉, 柿内秀樹, 百島則幸, N.Baglan, 杉原真司, 宇田達彦:【研究報告】質量分析法と燃焼－ LSC 法による植物中の組織結合型トリチウム測定」九州環境管理協会 会報 「環境管理」 第 40 号, 49-53(2011).

[141] Jean-Baptiste, P. et al., ^{3}He Mass Spectrometry for Very Low-Level Measurement of Organic tritium in Environmental Samples. *J. Environ. Radioact.*, **101**, 185-190 (2010).

Because the contribution of helium from air cannot be completely excluded in ^{3}He measurement via noble-gas mass spectrometry, a correction must be made based on the ratio of ^{3}He to ^{4}He ($^{3}He/^{4}He$) obtained by analyzing air samples.

In the measurement of ^{3}He via noble-gas mass spectrometry, there is no need to perform operations such as the purification of water samples or decomposition of organic matter. Hence, analysis can be performed nondestructively without altering samples. Additionally, because of the need for special storage containers and precise and expensive mass spectrometers, this analytical method has not been widely used to quantify tritium.

Figure D.2 Sealed container containing biological samples

Figure D.3 Noble-gas mass spectrometer (Gas purification line in the front and mass spectrometer in the back)

Appendix

Appendix A Nuclear Data for Tritium

Nuclear data utilized for radioactivity calculation should be extracted from reliable nuclear data collections, and the nuclear data used should be included with the analysis results. For an example of nuclear data collection, refer to Chapter 6 "Nuclear Data" in the Radioactivity Measurement Methods Series No. 7 " Gamma-ray Spectrometry using Germanium Semiconductor Detector."

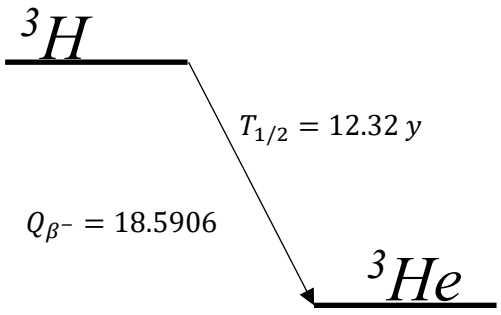
The nuclear data for tritium used in this measurement method were obtained from the Evaluated Nuclear Structure Data File (ENSDF) maintained by the National Nuclear Data Center (NNDC) in the United States. The data are shown in Appendix Table 1.1. In addition, a tritium decay diagram is presented in Appendix Figure 1.1.

Appendix Table 1.1 Tritium nuclear data

Half life (year)	β-ray maximum energy (keV)	Decay mode (emission rate (%))
12.32 ± 0.02	18.5906 ± 0.0032	β− (100)

*1 Source of nuclear data is ENSDF (as of September 2022).

*2 Half life and maximum energy of β-rays are listed, along with their uncertainties.



Appendix Figure 1.1 Tritium decay mode

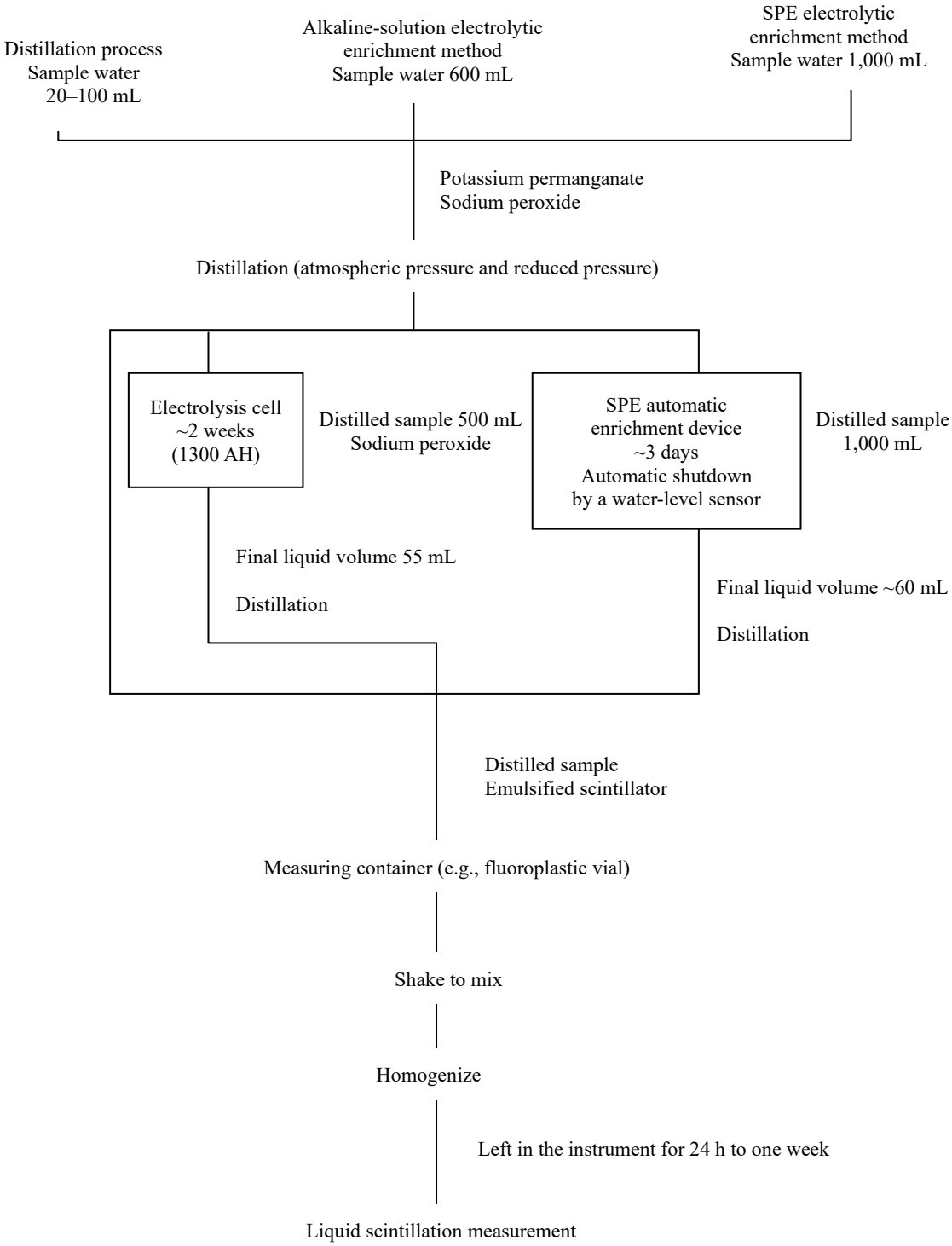
Appendix B Explanation of Terms

Term	Description
Quenching	Quenching effect. A decrease in scintillator luminescence due to various factors. There are different types of quenching: chemical quenching, color quenching, oxygen quenching, and concentration quenching.
Counting rate	Total counting per unit time. It is usually expressed in cpm (count per minute) or cps (count per second).
Gain	Value characterizing the amplification of an input signal by an amplifier.
Decision threshold	The boundary value in the background distribution when the probability of a type-I error (mistakenly determining that a physical effect exists in background measurements) is set to α in the calculation of the lower detection limit according to ISO 11929.
Lower detection limit	Minimum amount that can be detected. Kaiser method, ISO 11929 (Currie method), and Copper method are used to calculate the lower detection limit.
Best estimation value	A mathematical estimation of the statistically most probable value.
Silica gel	A gel made of silicon dioxide. In this manual, a hygroscopic agent is used to collect HTO from the atmosphere.
Tritium	An isotope of hydrogen with a mass number of 3, also called triple hydrogen, a pure β-ray emitter, with a half life of 12.32 years and a maximum β-ray energy of 18.6 keV.
Emulsified scintillator	It is a scintillator that absorbs radiation energy, such as β-rays, and emits fluorescence, to which an emulsifier is added, and is used here for analyzing tritiated water.
Half life	The time it takes for radionuclides to decrease their radioactivity to half the amount at a reference time. The half life depends on nuclides and can be much shorter than one second for shortest nuclides and billions of years or more for longest ones. Let the half life be T, elapsed time be t, and radioactivity at the reference time ($t = 0$) be A_0, then radioactivity A at time t is expressed as follows: $A = A_0 e^{-\lambda t}$ or $A = A_0 \left(\frac{1}{2}\right)^{t/T}$ Note that $\ln(2) \fallingdotseq 0.693$ and that the relationship between the half life and decay constant λ is $T = \ln(2)/\lambda$.
Uncertainty	The range of variation that is statistically acceptable for obtained measurement results. Combined uncertainty includes uncertainties associated with measurements, such as the uncertainty of counting (customarily counting error), uncertainty of efficiency used in measurements, and uncertainty of

Term	Description
	weighing samples used in analyses. However, it is not always necessary to combine all uncertainties because they are very small or difficult to estimate.
Molecular sieve	It is a hydrous metal salt of synthetic crystalline aluminosilicate. In this manual, a hygroscopic agent is used to collect HTO from the atmosphere.
E_n Number	A method used to evaluate the skills of a testing laboratory. It is expressed by the following equation: If the absolute value is less than 1, performance is considered satisfactory. $$En = \frac{Analysis\ value_{lab} - Analysis\ value_{ref}}{\sqrt{{U_{lab}}^2 + {U_{ref}}^2}}$$ U_{lab}: expanded uncertainty of participating laboratory (coverage factor k = 2) U_{ref}: expanded uncertainty of the reference laboratory or assigned value (coverage factor k = 2)
OBT	Organically Bound Tritium (OBT) in a biological sample. It is contained in water recovered by drying samples, removing tissue-free water, and then burning it. It is classified into two types: the exchangeable type, which bonds to oxygen or nitrogen atoms and readily exchanges with hydrogen, and nonexchangeable type, which bonds to carbon chains and is not easily exchanged.
TFWT	Tissue-Free Water Tritium (TFWT) in a biological sample. It is contained in water recovered via vacuum freeze drying.

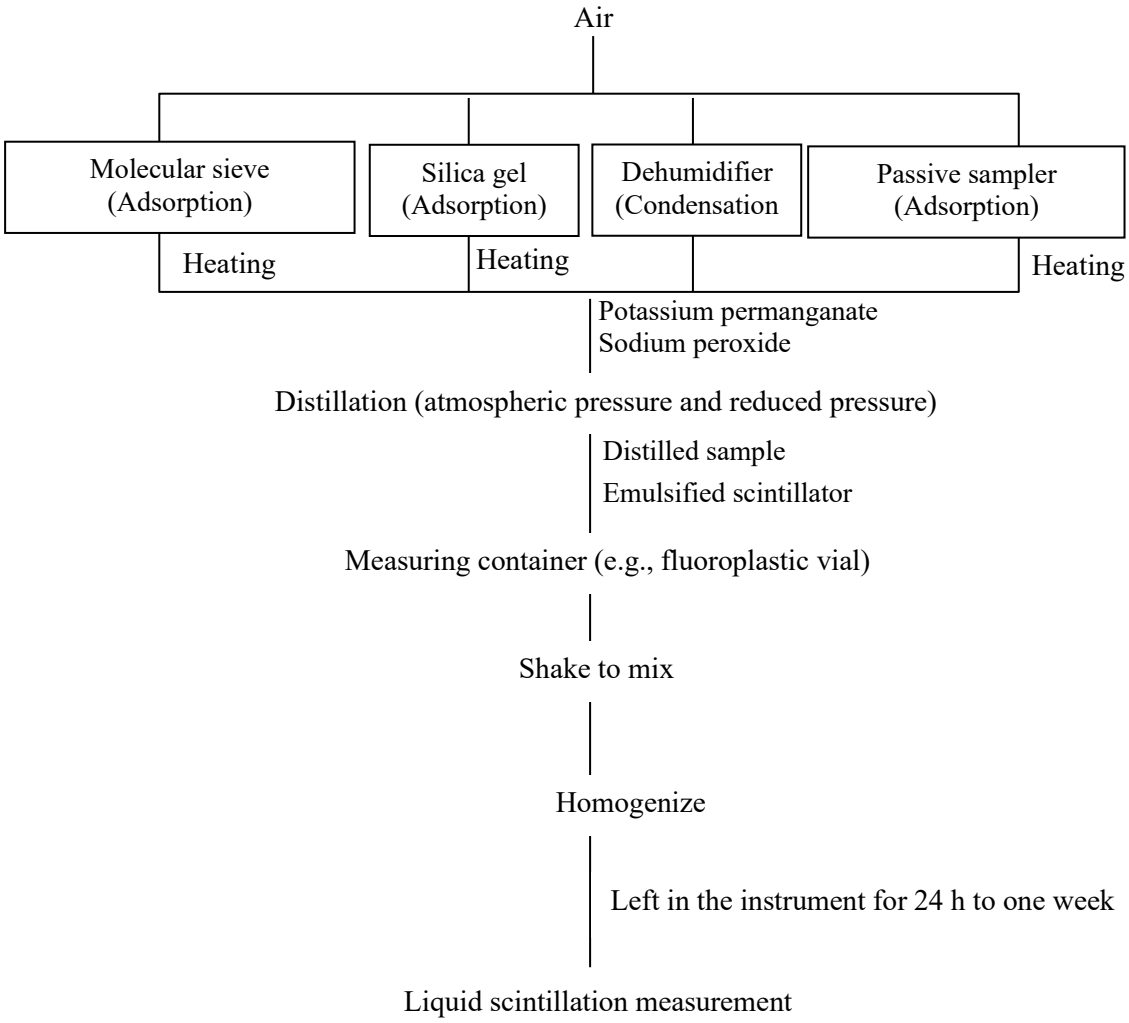
Appendix C Analysis Flow

(1) Water samples

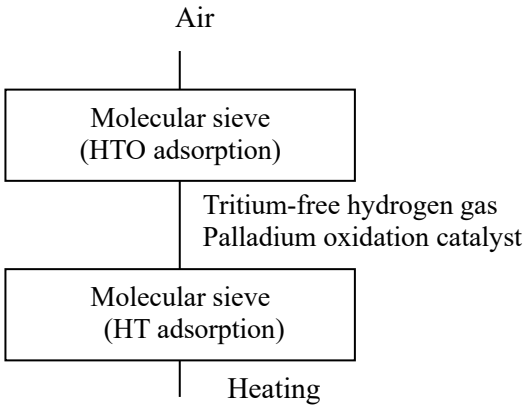


(2) Atmospheric sample

1) HTO

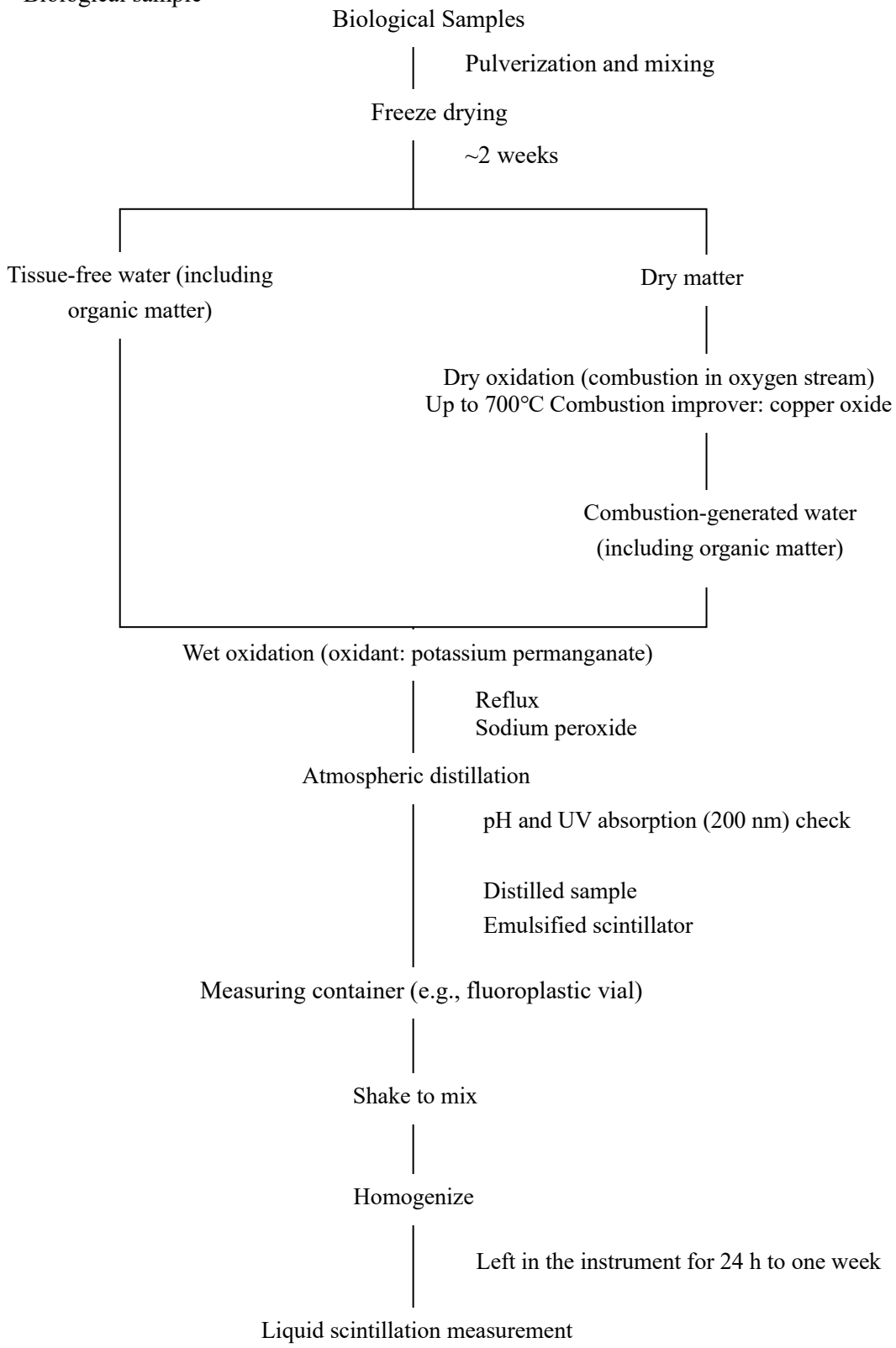


2) Hydrogen–tritium



* Same as the heating operation and thereafter of (1) HTO.

(3) Biological sample



References

1) 宇田達彦，田中将裕：小特集 施設起源トリチウムの移行モデルと環境トリチウム分布. 2.環境トリチウムの現状と分布．2.1 大気中トリチウム濃度の変遷と化学形態別測定, *J. Plasma Fusion Res.*, **85(7)**, 423-425 (2009).
2) IRSN. Radionuclide sheet: Tritium and the Environment (2010).
3) UNSCEAR. *Sources and Effects of Ionizing Radiation*, UNSCEAR 2000 Report to the General Assembly, with Scientific Annexes, Volume I: Sources, Annex A: Dose Assessment Methodologies (2000).
4) 柿内秀樹：小特集 トリチウム分離・濃縮技術．4.環境分析のためのトリチウム電解濃縮, *J. Plasma Fusion Res.*, **92(1)**, 26-30(2016).
5) UNSCEAR. *Sources, Effects and Risks of Ionizing Radiation*, UNSCEAR 2016 Report to the General Assembly, with Scientific Annexes, Annex C: Biological effects of selected internal emitters—Tritium (2016).
6) Ministry of Economy, Trade and Industry. Disposal of ALPS Treated Water. https://www.meti.go.jp/earthquake/nuclear/hairo_osensui/alps.html
7) The Cabinet Meeting on Contaminated Water, Treated Water and Decommissioning issues. (2021). *Basic Policy for Handling of ALPS Treated Water at the TEPCO's Fukushima Daiichi Nuclear Power Station*. https://www.meti.go.jp/earthquake/nuclear/hairo_osensui/alps_policy.pdf
8) The Nuclear Regulation Authority. The Guideline for Emergency Preparedness and Response. (Partially revised on July 6, 2022)
9) The Secretariat of the Nuclear Regulation Authority. Ordinary Monitoring (Supplementary Reference Materials for The Guideline for Emergency Preparedness and Response) (Revised December 21, 2021)
10) JIS Q 17043: Conformity Assessment - General Requirements for Proficiency Testing (2011).
11) 徳山秀樹，吉田暁美：夜光時計から漏洩した水蒸気状トリチウムの水への移行, *RADIOISOTOPES*, **47**, 560-562(1998).
12) N. Momoshima, T. Yamaguchi, T. Toyoshima, Y. Nagao, M. Takahashi, M. Takamura, Y. Nakamura, Tritium in the Atmospheric Environment, *Journal of Nuclear and Radiochemical Sciences*, **8(2)**, 117-120 (2007).
13) 村田敏，榎本敏夫，宮内樹代史：シリカゲル薄層の吸湿特性と固定層のシミュレーション, *農業機械学会誌*, **55(3)**, 41-49(1993).
14) N. Akata, H. Kakiuchi, K. Kanno, N. Shima, S. Hisamatsu, Determination of the Atmospheric HTO Concentration Around the Nuclear Fuel Reprocessing Plant in Rokkasho by Using a Passive Type Sampler, *Fusion Sci. Technol.*, **60(4)**, 1292-1295 (2011).
15) 玉利俊哉，島長義，百島則幸： 線量評価のための魚介類中トリチウム迅速分析法, *保健物理*, **55 (3)**, 136-143 (2020).
T. Tamari, N. Shima, N. Momoshima, (Secondary Publication) Rapid Tritium Analysis Method in Seafood Dose Evaluation, *Jpn. J. Health Phy.*, **59(2)**, 88~94 (2024)
16) 日本食品標準成分表 2020 年版（八訂）： 文部科学省 科学技術・学術政策局政策課資源室（https://www.mext.go.jp/a_menu/syokuhinseibun/mext_01110.html）
17) 平宏和：食品図鑑, 女子栄養大学出版部(2006).

18) JIS Z 8404-1: Measurement Uncertainty - Part 1 (2008).
19) J. A. Cooper, Factors Determining the Ultimate Detection Sensitivity of Ge (Li) Gamma-Ray Spectrometers. *Nucl. Instrum. Methods*, **82**, 273-277 (1970).
20) H. Kaiser, Zum Problem der Nachweisgrenze. *Analytisehe Chemie*, 209,1-18 (1965).
21) L.A. Currie, Limits for Qualitative Detection and Quantitative Determination Application to Radiochemistry. *Anal. Chem.,* **40**, 586-593 (1968).
22) ISO 11929-4:2022 Determination of the Characteristic Limits (Decision Threshold, Detection Limit and Limits of the Coverage Interval) for Measurements of Ionizing Radiation — Fundamentals and Application — Part 1: Elementary Applications (2022).
23) B. Kumar et al. A Compact Tritium Enrichment Unit for Large Sample Volumes with Automated Re-Filling and Higher Enrichment Factor. *Appl. Radiat. Isot.*, **118**, 80-86 (2016).
24) 北野寛:日本における国家計量標準とその供給体制：湿度標準, *計測と制御*, **48(4)**, 346-348（2009）.
25) JIS Z 8806: Humidity - Measurement Methods (2001).
26) 芝亀吉：湿度とその測定法, *高分子*, **7(1)**, 53-56（1958）.
27) H. Kuwata, T. Misono, K. Fujiwara, M. Takeishi, S. Manabe, A. Kitamura. Rapid Tritium Analysis for Marine Products in the Coastal Area of Fukushima. *Radiat. Environ. Med.*, **9(1)**, 28-34 (2020).
28) ISO 11929-4:2022, Determination of the Characteristic Limits (Decision Threshold, Detection Limit and Limits of the Coverage Interval) for Measurements of Ionizing Radiation — Fundamentals and Application — Part 4: Guidelines to Applications. ISO 11929-4:2022 (2022).
29) V. Thu Bac et al. Study to Build up Method for Determining Radioactivity of h-3 in Atmosphere. Annual Report for 2014 (VINATOM-AR 14-11), 109-117 (2015).
30) ISO 20041-1: Tritium and carbon-14 activity in gaseous effluents and gas discharges of nuclear installations — Part 1: Sampling of tritium and carbon-14 (2022).
31) 小嵐淳ら：排気中トリチウムモニタリング手法の検証（再評価）と高度化への提言,核燃料サイクル開発機構 東海事業所 技術報告（JNC TN8410 2005-004）(2005).
32) T. Tamari et al., OBT Measurement of Vegetation by Mass Spectrometry and Radiometry. *Fusion Sci. Technol.*, **60(4)**, 1252-1255 (2011).
33) 柿内秀樹, 赤田尚史: 原子力関連施設周辺での環境トリチウムモニタリングの実際, *J. Plasma Fusion Res.* **89(10)**, 645-651(2013) .
34) H. Kakiuchi et al., Low-Level Measurement with a Noble Gas Mass Spectrometer for Organically Bound Tritium in Environmental Samples. *Fusion Sci. Technol.*, **60(4)**, 1256-1259 (2011).
35) 玉利俊哉, 柿内秀樹, 百島則幸, N.Baglan, 杉原真司, 宇田達彦:【研究報告】質量分析法と燃焼－ LSC 法による植物中の組織結合型トリチウム測定」九州環境管理協会 会報 *「環境管理」* 第 40 号, 49-53(2011).
36) P. Jean-Baptiste et al., ^{3}He mass spectrometry for very low-level measurement of organic tritium in environmental samples, *J. Environ. Radioact.*, **101**, 185-190 (2010).

Revision history
Established in October 1977
Revised March 1996
Revised July 2002
Revised October 2023