The Series of Environmental Radioactivity Measuring Methods

AN-C
(No.25)

Radiocarbon Analysis

Amendment of June 2025
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

Introduction 1

Chapter 1 Atmosphere 3
1.1 Sample collection 3
1.1.1 Sample collection volume 3
1.1.2 Precautions during sample collection 3
1.2 Sample collection methods 3
1.2.1 Equipment, instruments, and reagents 3
1.2.2 Procedure 4
1.3 Sample preparation 4
1.3.1 Equipment, instruments, and reagents 5
1.3.2 Procedure 5

Chapter 2 Water 7
2.1 Sample collection 7
2.1.1 Sample collection volume 7
2.1.2 Precautions during sample collection 7
2.2 Sample preparation 7
2.2.1 Equipment, instruments, and reagents 8
2.2.2 Procedure 9

Chapter 3 Soil 11
3.1 Sample collection 11
3.1.1 Sample collection volume 11
3.1.2 Precautions after sample collection 11
3.2 Sample preparation 11
3.2.1 Equipment, instruments, and reagents 11
3.2.2 Procedure 13

Chapter 4 Biological Samples 15
4.1 Sample collection 15
4.1.1 Sample collection volume 15
4.2 Sample preparation 15
4.2.1 When using a sample combustion system 15
4.2.1.1 Equipment, instruments, and reagents 15
4.2.1.2 Procedure 16
4.2.2 When using a rapid sample combustion system 16
4.2.2.1 Equipment, instruments, and reagents 16
4.2.2.2 Procedure 17

Chapter 5 Measurement 20
5.1 Preparation of blank measurement samples 20
5.1.1 Equipment, instruments, and reagents 20
5.1.2 Procedure 21
5.2 Preparation of standard samples for counting efficiency determination 23
5.2.1 Wet decomposition method 23
5.2.1.1 Equipment, instruments, and reagents 23
5.2.1.2 Procedure 24
5.2.2 Wet decomposition method using a commercially available benzene synthesis system 26
5.2.2.1 Equipment, instruments, and reagents 26
5.2.2.2 Procedure 26
5.2.3 Dry decomposition method 27
5.2.3.1 Equipment, instruments, and reagents 27
5.2.3.2 Procedure 28
5.3 Liquid scintillation counting using the benzene synthesis method 31
5.3.1 Procedure when using a custom-built benzene synthesis system 33
5.3.1.1 Equipment, instruments, and reagents 33
5.3.1.2 Procedure 34
5.3.2 Procedure when using a commercially available benzene synthesis system 46
5.3.2.1 Equipment, instruments, and reagents 46
5.3.2.2 Procedure 47
5.3.3 Measurement 52
5.3.3.1 Equipment, instruments, and reagents 52
5.3.3.2 Setting of measurement conditions 54
5.3.3.3 Preparation and measurement of samples 55
5.3.4 Calculation of specific radioactivity of ^{14}C 56
5.4 Liquid scintillation measurement method using carbon dioxide absorption 57
5.4.1 Preparation of measurement samples 57
5.4.1.1 Equipment and instruments 57
5.4.1.2 Procedure 58
5.4.2 Measurement 60
5.4.2.1 Equipment, instruments, and reagents 60
5.4.2.2 Setting of measurement conditions 60
5.4.2.3 Sample measurement 60
5.4.3 Calculation of specific radioactivity of ^{14}C 61
5.5 Uncertainty 63
5.6 Lower detection limit 63

Chapter 6 Quality Assurance 65

6.1 Internal quality control 65
6.1.1 Traceability 65
6.1.2 Routine inspection 65
6.2 External quality control 67
6.2.1 Interlaboratory comparison 67
6.2.2 Proficiency testing 67

Explanation 69
Explanation A Specific radioactivity of ^{14}C of NIST oxalic acid 71
Explanation B Example of uncertainty evaluation 73
Explanation C Examples of activity concentration and lower detection limit calculations 89

Information 103
Information A Accelerator mass spectrometry 105

Appendix 113
Appendix A Nuclear data 115
Appendix B Terminology 116
Appendix C Results of cross-check between analytical methods 118
Appendix D Units and isotopic fractionation effects 120

References 123

Introduction

This measurement method specifies procedures for the analytical measurement of radiocarbon (^{14}C; half-life: 5,700 years; maximum beta-particle energy: 156.475 keV).

The main sources of ^{14}C are: (1) interactions between cosmic rays and nitrogen atoms, (2) atmospheric nuclear weapon testing, and (3) activation reactions involving nitrogen and other elements in nuclear reactors. In case (3), ^{14}C is released through processes such as the reprocessing of spent fuel[*1]. Approximately 1.4 PBq (P [peta] = 10^{15}) of ^{14}C is produced annually by cosmic rays, and the total global inventory is approximately 8,500 PBq. The majority of this inventory exists in the oceans, while approximately 140 PBq is present in the atmosphere. Atmospheric nuclear weapon testing were conducted frequently during the 1950s and 1960s, releasing approximately 350 PBq of ^{14}C into the atmosphere[*2,*3]. When large amounts of ^{14}C are introduced into the atmosphere, the specific radioactivity of ^{14}C in atmospheric carbon dioxide (CO_2) increases sharply. By the mid-1960s, it had reached approximately 1.5–2 times the level before atmospheric nuclear weapon testing. Since then, owing to the cessation of atmospheric nuclear weapon testing and the supply of "dead carbon" (carbon containing no ^{14}C) from the combustion of fossil fuels (the Suess effect), the specific radioactivity of ^{14}C in the atmosphere has been decreasing. In contrast, the total amount of ^{14}C released worldwide from reprocessing plants is approximately 2 PBq, and its effect is extremely small when compared with releases from atmospheric nuclear weapon testing[*3].

^{14}C is one of the radionuclides monitored under routine monitoring programs, as it is used to estimate and evaluate radiation doses to residents living around reprocessing plants[*4]. This measurement method was established for local governments, operators, research institutions, etc. to conduct environmental radiation monitoring near nuclear facilities, including nuclear power plants and reprocessing plants. The initial edition was promulgated in 1993, nearly three decades ago.

Furthermore, ^{14}C is utilized in diverse research fields. In the field of environmental studies, it functions as a natural tracer for source identification and for elucidating the transport and behavior of various substances of natural and anthropogenic origin. In archaeology, radiocarbon is used for dating, taking advantage of the fact that CO_2 is incorporated into plants through photosynthesis and transferred to animals via the food chain and that the ^{14}C content decreases after their death[*5].

Under this revision, the principal analytical techniques retained are liquid scintillation counting using the benzene synthesis method and the CO_2 absorption method. In addition, accelerator mass spectrometry, which enables highly accurate measurements using small sample quantities, has been newly described as a reference method.

The measurement targets addressed in this method are the atmosphere, water, soil, and biological samples. Radiation doses to humans from ^{14}C are calculated by multiplying the specific radioactivity of ^{14}C, carbon content in the ingested material, intake amount, and dose conversion

---

[*1] 岩倉哲男：原子力施設からの^{14}C, 日本原子力学会誌, Vol. 35, No. 10, 874 (1993)

[*2] United Nations Scientific Committee on the Effects of Atomic Radiation：UNSCEAR 2008 Report (2010)

[*3] Journal of Environmental Radioactivity 166 (2017) 56-66

[*4] 原子力規制庁監視情報課：平常時モニタリングについて（原子力災害対策指針補足参考資料），（Rev. March 21, 2024)

[*5] 近藤美由紀：環境研究における自然トレーサーとしての放射性炭素（^{14}C）の利用，国環研ニュース，33 巻，6号 (2015)

factor. Accordingly, measurement results are expressed as the specific radioactivity of ^{14}C in becquerels per gram of carbon (Bq/gC). Other expression formats, such as permille (‰) and percent modern carbon (pMC), are also introduced[*6].

In recent years, there has been an increasing demand to ensure the reliability of analytical capabilities in radioactivity analysis, as well as its objectivity and transparency.

Therefore, this revision includes descriptions of the estimation of analytical uncertainty, participation in interlaboratory comparisons and proficiency testing, and the calculation of lower detection limits.

Although this measurement method describes standard techniques used in environmental radiation monitoring, it does not restrict the adoption of new or emerging technologies, including advances in analytical methods. Analytical methods should be selected in accordance with the analytical objectives and the required level of accuracy. To assist in selecting analytical methods, Introductory Table 1 presents the detectable levels for each method. Because detectable levels vary depending on the measuring instrument and the measurement container, they should be regarded as reference values .

Guidelines for selecting each measurement method are outlined below.

Benzene synthesis method:

Samples are pretreated using a vacuum line and measured with a liquid scintillation counter. This method enables highly accurate analysis and is suitable for environmental radiation monitoring.

CO_2 absorption method:

Samples are pretreated using commercially available equipment and measured with a liquid scintillation counter. This method allows simple analysis and is suitable for purposes of environmental radiation monitoring, including screening.

Introductory Table 1 Comparison of detectable levels for each analytical method

Analytical method	Detectable level (Bq/gC)
Benzene synthesis method※1	0.002
CO_2 absorption method※2	0.02

※1 Carbon content: 1.7 g; counting efficiency: 75%; background counting rate: 0.3 cpm; measurement time: 500 min.

※2 Carbon content: 1.0 g; counting efficiency: 55%; background counting rate: 11 cpm; measurement time: 500 min.

[*]6 熊本雄一郎、荒巻能史：海洋観測ガイドライン, Vol. 3, Chap. 9 (2015)

Chapter 1 Atmosphere

CO_2 in ambient air is the target for sampling.

Methods for collecting CO_2[*7] include using alkaline aqueous solutions (such as sodium hydroxide solution) or molecular sieves (4A) as absorbents. Ambient air is passed through the absorbent using an air pump to capture CO_2. By recording the atmospheric intake volume (m^3), the specific radioactivity of ^{14}C (Bq/gC) and the ^{14}C activity concentration per unit volume (Bq/m^3) can be calculated. Sampling requires a power supply for the air pump, and the system condition must be checked periodically during the sampling period. Although this method requires considerable equipment for purposes such as sampling, power supply, and labor, it allows quantitative analysis.

1.1 Sample collection

1.1.1 Sample collection volume

The concentration of CO_2 in ambient air varies in the range of 0.6–0.8 g/m^3[*8]. Assuming an average of 0.2 gC/m^3 (approximately 390 mL/m^3), at least 5 m^3 of air must be drawn to collect 1 g of carbon. Because the carbon amount required varies depending on the analytical method, the air sampling volume must be determined according to the selected method. When using the benzene synthesis method, to obtain a sample volume equivalent to approximately 20 g of calcium carbonate (2.4 gC), an air sample volume of at least 12 m^3 is required.

1.1.2 Precautions during sample collection

The sample collection site should be a wide, flat area not strongly influenced by specified facilities[*9]. A rain shield should be installed to prevent rain droplets from entering during rainfall. If no suitable site is available, sampling may be conducted on a flat rooftop.

1.2 Sample collection methods

Sodium hydroxide solution is commonly used as the alkaline absorbent for collecting CO_2. When using sodium hydroxide, particular care must be taken during pH adjustment in the subsequent formation of calcium carbonate to prevent calcium hydroxide formation.

1.2.1 Equipment, instruments, and reagents

(1) Equipment

Not used.

(2) Instruments

1) Gas washing bottle: 500 mL or 1 L, glass filter (pore size No. G1)
2) Integrating flowmeter (dry type)

[*7] IAEA: Management of Waste Containing Tritium and Carbon-14, Technical Reports Series, No.421 (2004)

[*8] World Data Centre: The World Data Centre for Greenhouse Gases https://gaw.kishou.go.jp/ (As of 2023, based on a survey of the most recent 20 years)

[*9] Boilers, incinerators, thermal power plants, busy roads, etc.

3) Flowmeter: Capable of measuring flow rates of 0–5 L/min
4) Air pump: Equipped with flowmeter having adjustable flow rates of 0–5 L/min
5) Dust filter: For dust removal; equivalent to a pre-filter used in pure water systems
6) Silicone resin tubing

(3) Reagents

1) Sodium hydroxide[*10,*11]

Sodium hydroxide aqueous solution (12 w/v%): Dissolve 500 g of special-grade sodium hydroxide in 600 mL of degassed, boiled pure water[*12]. Seal the solution in a polyethylene bottle and let it stand for several days. Dilute the supernatant sevenfold with degassed pure water[*13]. Here, "pure water" refers to water purified by ion exchange or equivalent methods.

1.2.2 Procedure

(1) Fill one gas washing bottle with pure water and the other bottles with the required volume of alkaline absorbent solution. To collect CO_2 quantitatively, two bottles of 800 mL each or three bottles of 400 mL of 12 w/v% sodium hydroxide solution are required.
(2) Connect the components in this order using silicone resin tubing: dust filter, integrating flowmeter, air pump, flowmeter, gas washing bottle (pure water), and gas washing bottles containing sodium hydroxide solution (2–3 bottles) (see Figure 1-1).
(3) Switch on the air pump to draw ambient air through the system.
(4) Maintain a flow rate of 1–2 L/min until the required amount of CO_2 is collected (estimated from the cumulative aspirated air volume).
(5) Stop the air pump.
(6) Begin analysis immediately using the collected absorbent solutions. If transport or storage is necessary, transfer the solutions to polyethylene bottles, seal tightly, and store until analysis.

1.3 Sample preparation

The sodium hydroxide solution containing collected atmospheric CO_2 (from Section 1.2) is reacted with calcium chloride to obtain calcium carbonate.

---

*10 Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act—i.e., substances that may pose risks to workers or cause health impairment—must be clearly labeled, accompanied by Safety Data Sheets, and assessed for risk, including the implementation of appropriate risk-reduction measures. Employers must ensure that workers are informed about and trained in the safe handling of such substances.

*11 Substances subject to the Poisonous and Deleterious Substances Control Act—i.e., those posing a high risk of acute toxicity–related health hazards—must be stored and displayed in areas clearly labeled as "Non-Pharmaceutical Poisonous Substances" or "Non-Pharmaceutical Deleterious Substances." Appropriate measures must be taken to prevent theft, loss, leakage, or similar incidents.

*12 Exercise caution, as heat is generated during handling.

*13 For preparation, quickly rinse the surface of granular sodium hydroxide with degassed cold pure water, then dissolve it in an equal volume of pure water. After cooling, seal the container tightly and leave it for several days to allow poorly soluble sodium carbonate to precipitate. Dilute the supernatant with degassed pure water before use.

1.3.1 Equipment, instruments, and reagents

(1) Equipment

1) pH meter
2) Drying oven

(2) Instruments

1) Filtration tool: Büchner funnel (9 cm diameter)
2) Suction flask
3) Glass rod
4) Filter paper: No. 5C (9 cm diameter)
5) Porcelain dish
6) Aluminum laminate bag
7) Desiccator

(3) Reagents

1) Ammonium chloride: Special grade
2) Calcium chloride: Special grade, anhydrous or dihydrate

・ Hot saturated calcium chloride solution: Dissolve calcium chloride in pure water with heating. Use the supernatant after undissolved calcium chloride has settled.

1.3.2 Procedure

(1) Transfer the solutions from the gas washing bottle (pure water) and sodium hydroxide bottles (No. 1 and No. 2) into a 3 L beaker. Rinse the bottles with water and add the washings to the beaker. Add pure water to bring the total volume to 2.5 L.
(2) Stir the solution thoroughly, add ammonium chloride, and adjust the pH to 10.5 using a pH meter.
(3) Heat the solution and, while stirring, add calcium chloride gradually to form a calcium carbonate precipitate. Approximately 9.3 g of calcium chloride is required per 1 g of collected carbon.
(4) Heat and age the precipitate[*14]. After settling, add 2–3 drops of the hot saturated calcium chloride solution to the supernatant and confirm that the supernatant does not become turbid. If turbidity occurs, repeat step 3.
(5) Filter the precipitate by suction using a Büchner funnel with No. 5C filter paper (measure dry tare weight) and wash with pure water.
(6) Place the filter paper in a porcelain dish, dry in an oven at 110°C for at least 4 h, measure the dry weight, seal in an aluminum laminate bag, and store in a desiccator.

[*]14 Note that when forming the calcium carbonate precipitate, if aging is insufficient, the precipitate may pass through No. 5C filter paper during filtration.

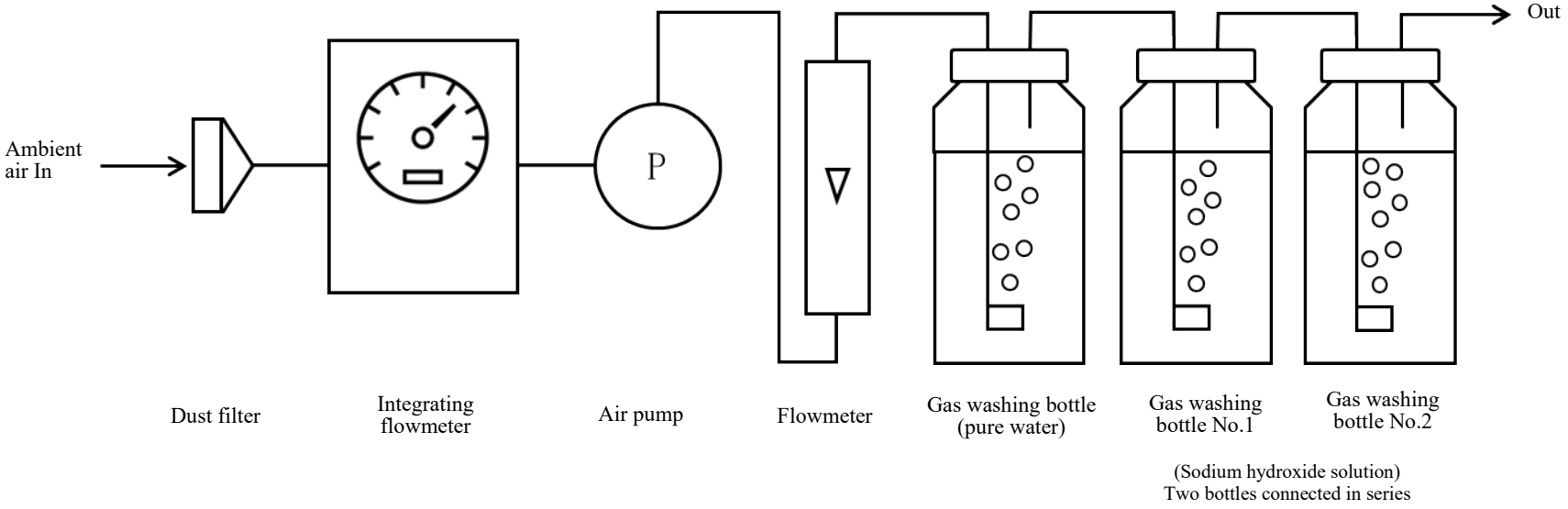


Figure 1-1 System for collecting CO_2 from ambient air

Chapter 2 Water

In water, inorganic carbon generally exists as HCO_3^-, depending on pH. After acidification with sulfuric acid, it can be expelled as CO_2 by purging with nitrogen gas. The inorganic carbon amount varies with the sample type. Seawater contains approximately 140 mg/L HCO_3^-, whereas river and lake water generally contain considerably lower amounts.

Groundwater varies widely, with concentrations ranging from 10 to 800 mg/L[*15]. For groundwater, the specific radioactivity of ^{14}C may change over time due to physical decay and the input of dead carbon.

Except for seawater, it is advisable to determine the inorganic carbon content in advance to estimate an appropriate sample volume.

Carbon in water samples is broadly categorized as inorganic or organic. Because organic carbon is typically present only in small amounts, the two forms are usually assessed together. In this method, inorganic and organic carbon are analyzed collectively without separation.

2.1 Sample collection

For water sampling methods, refer to The Series of Environmental Radioactivity Measuring Methods No. 16, “Method for Sampling of Environmental Materials,” and No. 35, “Generic Procedures for Environmental Sampling in Emergencies.”

2.1.1 Sample collection volume

Although carbon content varies by sample, recovering 1 g of carbon generally requires at least 100 L of water. For inland waters (rivers and lakes) and drinking water (tap and groundwater), collect at least 200–300 L, including volumes for analysis and storage. The sample volume should be determined according to the carbon amount required by the selected analytical method.

2.1.2 Precautions during sample collection

Store samples in tightly sealed containers (e.g., polyethylene tanks) to prevent evaporation and contamination by atmospheric CO_2. Do not add acid at the time of collection.

2.2 Sample preparation

Acidify the collected sample with concentrated sulfuric acid, expel CO_2 by passing nitrogen gas through the sample (see Figure 2-1), and collect it in ammonia water. Sodium hydroxide solution may be used as an alternative alkaline solution. The procedure requires approximately 8–9 h per sample.

*15 石井雅男, 吉川久幸, 松枝秀和：電量滴定法による海水中の全炭酸濃度の高精度分析及び大気中の二酸化炭素と海水中の全炭酸の放射性炭素同位体比の測定，気象研究所技術報告第41号，1-71（2000）

To avoid isotopic exchange during storage, it is desirable to immediately fix carbon as carbonate and store it in aluminum laminate bags or similar containers.

2.2.1 Equipment, instruments and reagents

(1) Equipment

1) Water sample tank: 100 L,
   Material: Transparent polyvinyl chloride (5 mm thick),
   Dimensions: Diameter Ø 460 mm, height 700 mm;
   Features: Upper part includes sample access opening (approx. 200 mm) and vent pipe.
2) Drying oven

(2) Instruments

1) Gas washing bottles: 500 mL
2) Silicone resin tubing
3) Air pump with adjustable flow rate (0–10 L/min), equipped with a flow meter
4) Filtration tool: Büchner funnel (Ø 9 cm)
5) Suction flask
6) Glass rod
7) Filter paper: No. 5C (Ø 9 cm)
8) Porcelain dish
9) Aluminum laminate bag
10) Desiccator

(3) Reagents

1) Sulfuric acid[*16,*17,*18]: Special grade
2) Ammonia water[*16,*17,*18]: Special grade; mass fraction: 28.0%–30.0%

・ Ammonia water (1+1): Mix equal parts of pure water and ammonia water.

3) Calcium chloride: Special grade, anhydrous or dihydrate

・ Hot saturated calcium chloride solution: Dissolve calcium chloride in pure water with heating and use supernatant after undissolved calcium chloride settles.

4) Nitrogen gas: Purity of 99.999%.

---

[*]16 Class III substances under the Ordinance on Prevention of Hazards due to Specified Chemical Substances—i.e., substances that may cause acute poisoning in the event of large-volume leakage—require measures to reduce exposure concentrations, such as the installation of local exhaust ventilation systems.

[*]17 Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act—i.e., substances that may pose risks to workers or cause health impairment—must be clearly labeled, accompanied by Safety Data Sheets, and assessed through risk evaluations, including the implementation of appropriate risk-reduction measures. Employers must also inform and train workers in the safe handling of these substances.

[*]18 Substances regulated under the Poisonous and Deleterious Substances Control Act—i.e., substances with a high risk of acute toxicity and related health hazards—must be stored and displayed in areas clearly labeled as “Non-Pharmaceutical Poisonous Substances” or “Non-Pharmaceutical Deleterious Substances.” Measures must also be implemented to prevent theft, loss, leakage, and similar incidents）

2.2.2 Procedure

(1) Connect the water sample tank, air pump, and gas washing bottles using silicone resin tubing (see Figure 2-1).
(2) Pour 100 L of sample into the tank, and replace the air inside with nitrogen from a gas cylinder.
(3) Fill each of the four gas washing bottles with 200 mL of ammonia water (1+1).
(4) Add 300 mL sulfuric acid through the tank's gas outlet and immediately connect the tubing.
(5) Switch on the air pump and circulate nitrogen at approximately 5 L/min.
(6) Allow generated CO_2 to be absorbed into ammonia water in the gas washing bottles.
(7) After 4 h, switch off the air pump and transfer the ammonia water containing CO_2 to a 2 L beaker.
(8) Refill each gas washing bottle with 200 mL of freshly prepared ammonia water (1+1).
(9) Continue absorption for another 4 h at approximately 5 L/min, then combine the ammonia water with the previous 2 L beaker contents.
(10) Heat the combined solution and gradually add calcium chloride to form calcium carbonate precipitate (approximately 9.3 g per 1 g collected carbon).
(11) Heat and age the precipitate[*19]. After settling, add 2–3 drops of hot saturated calcium chloride solution to the supernatant to confirm no turbidity. If turbidity occurs, repeat step 10.
(12) Perform suction filtration of the precipitate using a Büchner funnel (filter paper No. 5C, with pre-measured dry tare weight) and a suction flask, and wash with pure water .
(13) Place the filter paper in a porcelain dish, dry in an oven at 110°C for at least 4 h. Measure dry precipitate weight (including filter paper), seal in an aluminum laminate bag, and store in a desiccator.

[*]19 Note: If the precipitate is not aged sufficiently, it may pass through No. 5C filter paper during filtration.

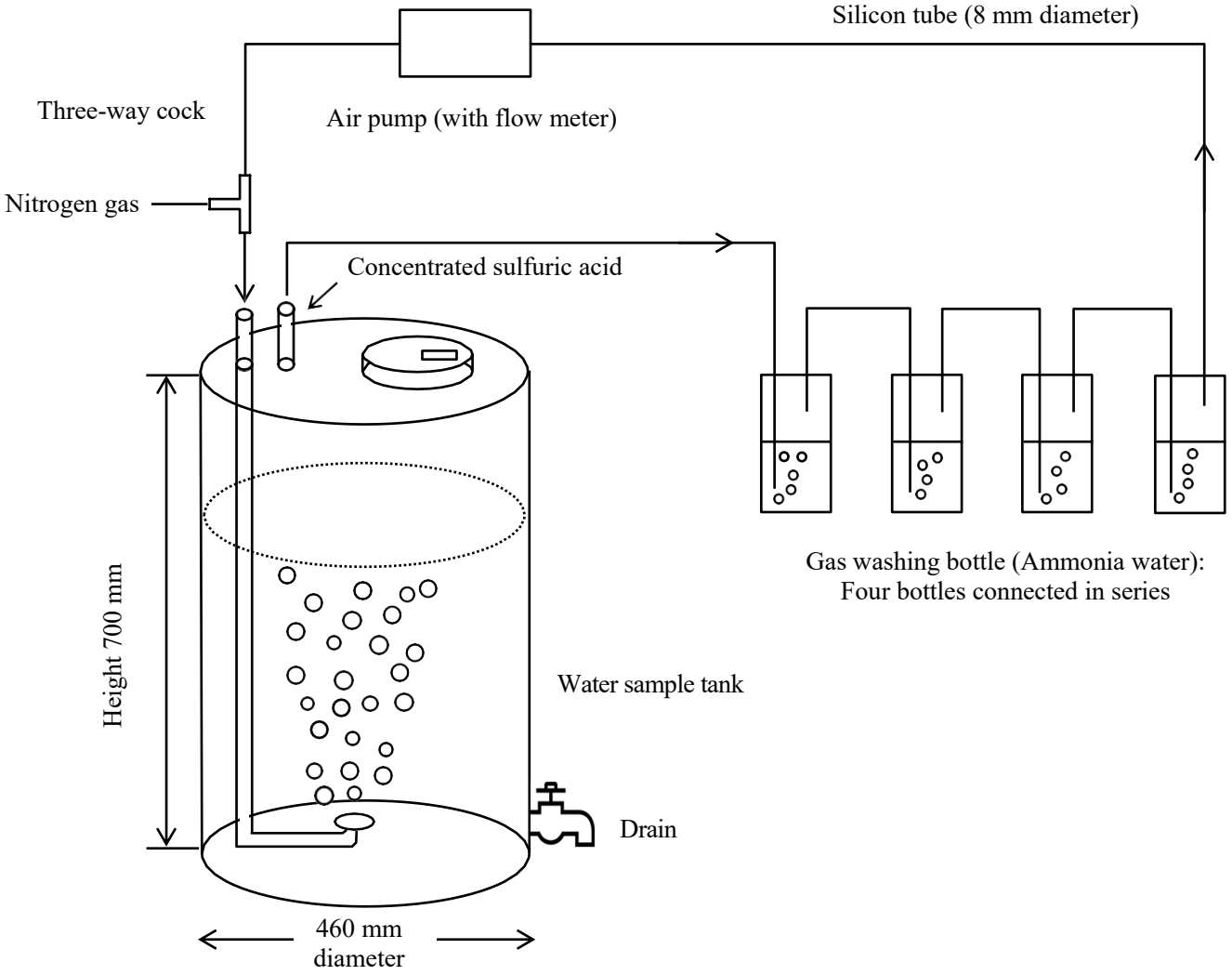


Figure 2-1 System for collecting CO_2 from water samples

Chapter 3 Soil

For soil samples, the target material is organic matter in the soil. Because this organic matter originates from decomposed plant material, it enables assessment of the transfer and accumulation of ^{14}C from vegetation.

After drying at a temperature low enough to avoid decomposition of organic matter, the sample is heated and combusted in an oxygen stream, causing the organic matter to oxidize into CO_2 and water. The generated CO_2 is then absorbed into an alkaline aqueous solution.

The organic matter content of soil depends on the amount of humus. It is relatively high in forest humus soils and cultivated soils but is almost absent in sand and similar materials. In general, the amount of organic matter cannot be determined simply by observing soil color. The same applies to riverbed and lakebed soils. Therefore, it is recommended to determine the approximate organic matter content in advance using methods such as wet and dry oxidation and then select an appropriate sample amount based on the results.

3.1 Sample collection

For methods of collecting soil samples, refer to The Series of Environmental Radioactivity Measuring Methods No. 16, "Method for Sampling of Environmental Materials," and No. 35, "Generic Procedures for Environmental Sampling in Emergencies."

3.1.1 Sample collection volume

To recover 1 g of carbon, at least 50 g of dry soil is required. The total amount of collected soil, including material for analysis and storage, should be at least 1–2 kg of fresh soil. Because the required amount of carbon varies depending on the analytical method, the sampling amount must be determined according to the selected method.

3.1.2 Precautions after sample collection

The collected soil should be dried in a drying oven set to a temperature (105°C) that does not cause decomposition of organic matter.

3.2 Sample preparation

For the treatment of soil samples, refer to The Series of Environmental Radioactivity Measuring Methods No. 16, "Method for Sampling of Environmental Materials." For humus soils containing large amounts of organic matter, it is preferable to first carbonize the sample at approximately 500°C in a nitrogen stream, followed by combustion.

3.2.1 Equipment, instruments and reagents

(1) Equipment

1) Sample combustion system: movable tubular furnace (see Figure 3-1)
2) Drying oven

(2) Instruments

1) Double-tube-type combustion tube (see Figure 3-1)
   Material: transparent quartz
   Dimensions: outer tube 1000 mm x Ø 45 mm; inner tube 500 mm x Ø 30 mm
2) Quartz wool
3) Gas washing bottles: 500 mL
4) Silicone resin tubing
5) Filtration tool: Büchner funnel (Ø 9 cm)
6) Suction flask
7) Glass rod
8) Filter paper: No. 5C (Ø 9 cm)
9) Porcelain dish
10) Aluminum laminate bag
11) Desiccator

(3) Reagents

1) Ammonia water[*20,*21,*22]: Mass fraction of 28.0%–30.0%

· Ammonia water (1+1): Mix equal parts of pure water and ammonia water.

2) Calcium chloride: Special grade, anhydrous or dihydrate

· Hot saturated calcium chloride solution: Dissolve calcium chloride in pure water with heating. Use the supernatant (saturated solution) while still hot after undissolved calcium chloride has settled.

3) Potassium permanganate[*23,*24]: Special grade

· Potassium permanganate solution (4 w/v%): Dissolve 4 g of potassium permanganate in 100 mL of pure water.

4) Copper oxide in the wire form[*20]
5) Oxygen gas (purity of ≥99.7%)
6) Nitrogen gas (purity of 99.999%)

---

[*]20 Hazardous substances requiring labeling under the Industrial Safety and Health Act (substances that may endanger workers or cause health impairment) must be clearly labeled, accompanied by Safety Data Sheets, and subjected to risk assessments, including the implementation of risk-reduction measures. Employers are required to inform and educate workers about the handling of these substances.

[*]21 Class III substances under the Ordinance on Prevention of Hazards due to Specified Chemical Substances (substances that may cause acute poisoning due to large-volume leakage): Measures must be taken to reduce exposure concentrations, such as installing local exhaust ventilation systems.

[*]22 Substances subject to the Poisonous and Deleterious Substances Control Act (those posing a high risk of acute toxicity-related health hazards): Storage and display areas must be labeled as "Non-Pharmaceutical Poisonous Substances" or "Non-Pharmaceutical Deleterious Substances," and necessary measures must be taken to prevent theft, loss, leakage, and similar incidents.

[*]23 Class II substances under the Ordinance on Prevention of Hazards due to Specified Chemical Substances (substances that cause chronic or delayed health effects, such as cancer): Measures must be taken to control sources of gas, vapor, or dust emissions, such as installing local exhaust ventilation systems.

[*]24 Classified as a Class I hazardous material (oxidizing solid) under the Fire Service Act. Care should be taken to avoid contact with strong acids, avoid storage with combustible materials, and avoid heating, impact, and friction.

3.2.2 Procedure

The operating procedure for using the double-tube-type combustion tube in combination with the sample combustion system shown in Figure 3-1 is described below.

(1) Accurately weigh approximately 100 g of dried fine soil and pack it into the inner combustion tube, with quartz wool packed at one end. Pack quartz wool at the other end as well, leaving gaps during packing. This prevents blockage of gas flow by generated moisture, tar, or similar substances.

(2) Loosely pack quartz wool over a length of approximately 10–20 cm in the afterburner section of the outer combustion tube (corresponding to electric furnace [B]).

(3) Place copper oxide, used as a combustion aid, in electric furnace (C).

(4) Connect the gas washing bottles in the following order:

Empty: An empty gas washing bottle to prevent backflow

$KMnO_4$: A gas washing bottle containing potassium permanganate solution for removal of sulfur oxides

Ammonia water: Gas washing bottles containing ammonia water (1+1) for CO_2 absorption (400 mL × 2 bottles)

Water: A gas washing bottle containing pure water for removal of ammonia[*25]

(5) Set the outer tube in the sample combustion system, insert the inner tube, and supply oxygen gas and nitrogen gas into the inner tube, and oxygen gas into the outer tube, each at approximately 50 mL/min. At this time, the pressure inside the tube becomes about +0.1 kg/cm^2 (approximately 0.01 MPa). If it exceeds +0.2 kg/cm^2 (approximately 0.02 MPa), this indicates an abnormal condition. In this case stop the operation and inspect the gas flow paths in the system.

(6) Raise the temperature of electric furnace (B) to 950°C–1000°C.

(7) Raise the temperature of electric furnace (C) to 700°C.

(8) Set the oxygen flow rates to 100 mL/min for the outer tube and 50 mL/min for the inner tube. Place electric furnace (A) at the right end of the inner tube and gradually raise its temperature over approximately 1 h. When the temperature reaches 700°C, slowly move electric furnace (A) while observing the combustion state.

There is generally no pressure difference between the outer and inner tubes, and the pressure rarely exceeds +0.2 kg/cm^2 (approximately 0.02 MPa). If a pressure difference occurs or the pressure becomes abnormally high, the operation should be stopped, as this condition is hazardous.

(9) After moving electric furnace (A) to the left end of the sample, raise its temperature to 1000°C and continue combustion for an additional 1 h[*26].

(10) After combustion is complete, transfer the ammonia water (1+1) from the two connected gas washing bottles to a 2 L beaker.

[*25] Because ammonia volatilizes from the upstream gas washing bottles used for carbon dioxide absorption, a water trap is employed to prevent its diffusion into the laboratory.

[*26] For samples containing large amounts of organic matter, rapid combustion may occur. Therefore, it is recommended to reduce the oxygen gas flow and mix in nitrogen gas while observing the combustion state.

(11) Heat the combined solution and, while stirring, gradually add calcium chloride to form a calcium carbonate precipitate. The required amount of calcium chloride is approximately 9.3 g per 1 g of collected carbon.

(12) Heat and age the precipitate[*27]. After the precipitate has settled, add 2–3 drops of hot saturated calcium chloride solution to the supernatant and confirm that no turbidity occurs. If turbidity is observed, the amount of calcium chloride added is insufficient; repeat step (11).

(13) Filter the precipitate by suction using a Büchner funnel (with No. 5C filter paper; measure dry tare weight) and a suction flask, and wash the precipitate with pure water.

(14) Place the filter paper in a porcelain dish, dry in an oven at 110°C for at least 4 h, After measuring the dry precipitate weight (including the filter paper), seal it in an aluminum laminate bag and store it in a desiccator.

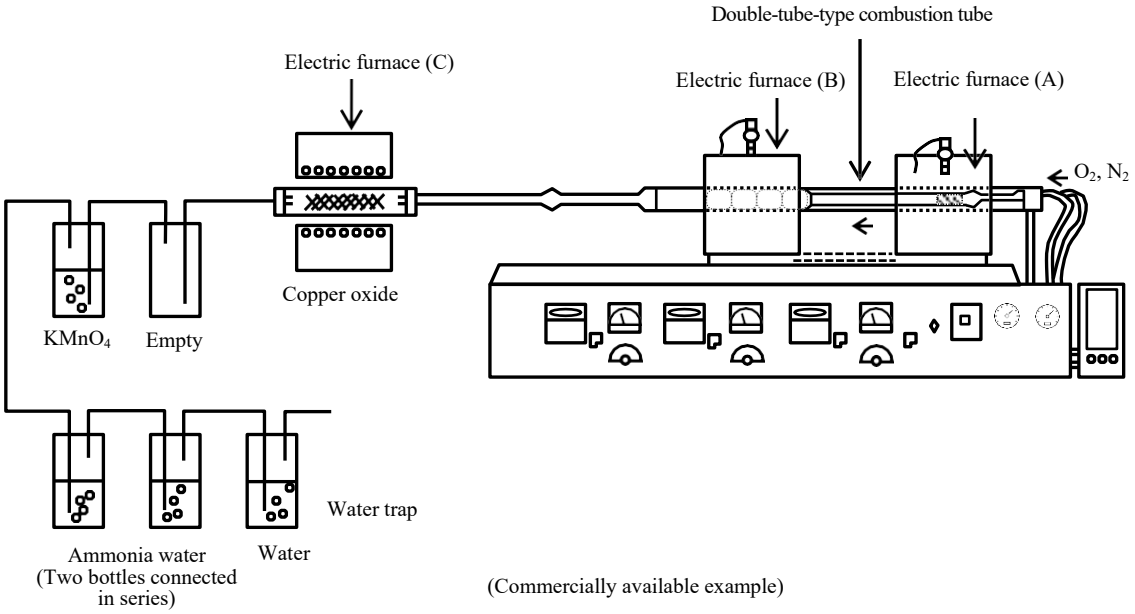


Figure 3-1 System used for sample combustion

[*]27 Note that during the formation of the calcium carbonate precipitate, insufficient aging may cause the precipitate to pass through No. 5C filter paper during filtration.

Chapter 4 Biological Samples

The target materials are organic matter in biological samples: agricultural, livestock, marine products, etc.

Samples are freeze-dried as needed to facilitate combustion, then heated and combusted in a flow of oxygen and nitrogen, thereby oxidizing the organic matter into CO_2 and water. The generated CO_2 is subsequently absorbed into an alkaline aqueous solution.

4.1 Sample collection

For methods of collecting biological samples, refer to The Series of Environmental Radioactivity Measuring Methods No. 16, "Method for Sampling of Environmental Materials," and No. 35, "Generic Procedures for Environmental Sampling in Emergencies."

4.1.1 Sample collection volume

To recover 1 g of carbon, a sample containing at least 3 g of dry matter is required. Depending on the water content, the sample weight should be at least 50–100 g of fresh material, including amounts required for analysis and storage. Because the required amount of carbon differs depending on the analytical method, the sampling amount must be determined according to the selected method.

4.2 Sample preparation

For biological samples, water is removed by vacuum freeze-drying if necessary, and the CO_2 produced by combustion is collected. However, as with soil samples, it is preferable to carbonize[*28] the samples prior to combustion[*29].

The time required for sample preparation is approximately 8–10 h per sample.

4.2.1 When using a sample combustion system

4.2.1.1 Equipment, instruments, and reagents

(1) Equipment

1) Homogenizer: Mixer, etc.
2) Freezer
3) Vacuum freeze dryer
4) Sample combustion system: movable tubular furnace (see Figure 3-1)
5) Drying oven

(2) Instruments

Same as 3.2.1(2).

(3) Reagents

[*28] Carbonization is not required when using a rapid sample combustion system.

[*29] The basic combustion procedure is the same as for soil samples. However, because biological samples consist largely of organic matter, it is advisable to first carbonize the sample at approximately 500°C in a nitrogen stream to prevent a sudden combustion reaction. After carbonization, the proportion of oxygen in the gas stream should be gradually increased, and complete ashing should finally be performed at 1000°C in a 100% oxygen stream.

Same as 3.2.1(3).

4.2.1.2 Procedure

(1) Biological samples (marine organisms, meat, vegetables, etc.) are thoroughly homogenized using a mixer.
(2) The homogenized sample is frozen in a freezer and then vacuum-dried using a vacuum freeze dryer*30.
(3) Record the mass of the sample daily after the start of drying, and continue drying until the mass becomes nearly constant (approximately 1 day to 1 week).
(4) The amount of fresh sample varies depending on its moisture content; weigh approximately 5–10 g of the dried sample (corresponding to approximately 2–4 g of carbon) and pack it into the inner combustion tube.
(5) Perform the procedures described in 3.2.2(2)–(14).

4.2.2 When using a rapid sample combustion system

In the benzene synthesis method using commercially available equipment, biological samples can be directly converted to CO_2 using a dedicated rapid sample combustion system (see Figure 4-1), and the generated CO_2 can be collected in the storage tank of the benzene synthesis system. This allows the process to proceed to the lithium carbide formation step without converting the CO_2 generated by combustion into calcium carbonate.

The approximate amounts of biological samples required to collect about 10 L of CO_2*31 necessary for benzene synthesis are as follows:

Rice: 17 g; raw milk (dry): 12 g; leafy vegetables (dry): 15 g; seaweed (dry): 15 g

4.2.2.1 Equipment, instruments, and reagents

(1) Equipment
1) Commercial rapid sample combustion system (Figure 4-1)
2) Commercial benzene synthesis system (Figure 5-8)

(2) Instruments
Not used.

(3) Reagents
1) Oxygen gas: Purity of ≥ 99.7%
2) Dry ice–alcohol coolant*32
3) Liquid nitrogen

*30 If the water in the sample does not need to be analyzed, the sample may be dried in a drying oven adjusted to 105°C instead of vacuum freeze-drying.
*31 Adjust so that the storage tank of the benzene synthesis system does not become positively pressurized.
*32 Ethanol cooled to −80°C with liquid nitrogen may also be used.

4.2.2.2 Procedure

(1) Place a sample into the sample combustion system so that the amount of CO_2 collected will be approximately 10 L.

(2) Connect an ignition fuse (10 cm long) between the terminals and position it so that the fuse lightly touches the sample.

(3) Inspect the O-ring of the sample combustion system, apply silicone grease to the O-ring, and install it.

(4) Securely attach the lid of the sample combustion system using the mounting fittings.

(5) Connect the coupling joint of the sample combustion system to Joint-1 of the benzene synthesis system body, and evacuate the air inside the sample combustion system.

(6) Using the dedicated regulator and gas charger, fill the sample combustion system with oxygen gas to approximately 20 kg/cm^2.

(7) After filling is complete, remove the gas charger and close the gas-charging valve and gauge valve of the sample combustion system.

(8) Connect one end of the ignition cable to the ignition terminal of the sample combustion system and the other end to the "10 cm terminal" of the ignition unit, then press the ignition switch to combust the sample.

(9) After the sample combustion system has cooled, connect its coupling joint to Joint-1 of the benzene synthesis system.

(10) Evacuate the CO_2 trap line of the benzene synthesis system, then close valve (V-9).

(11) Cool trap (T-1) with a dry ice–alcohol coolant, and cool traps (T-2) and (T-3) with liquid nitrogen.

(12) Open the exhaust valve of the combustion system extremely slowly. When the pressure on gauge (G-1) rises to −20 to −15 inHg[*33], slightly open valve (V-9) to exhaust and collect CO_2.

(13) When most of the gas in the combustion system has been exhausted and the pressure on gauge (G-1) decreases to −25 inHg, close valves (V-1), (V-5), and (V-9).

(14) Remove the liquid nitrogen from the traps, and while carefully monitoring the pressure change on gauge (G-5), open valve (V-9) to evacuate.

(15) Close valve (V-9), then sequentially open valves (V-11), (V-12), and (V-13) to store the CO_2 in the storage tank.

(16) After all CO_2 collected in the traps has vaporized, close valves (V-12) and (V-13), then cool the microtrap with liquid nitrogen to collect the CO_2 remaining in the traps and lines.

(17) After closing valve (V-11), open valves (V-12) and (V-13), remove the liquid nitrogen from the microtrap, and transfer the CO_2 to the storage tank.

Subsequent operations are the same as those for benzene synthesis described in Section 5.3.2.2(b).

[*]33 inHg means inches of mercury, which is the unit used in the commercially available benzene synthesis system adopted in this method.

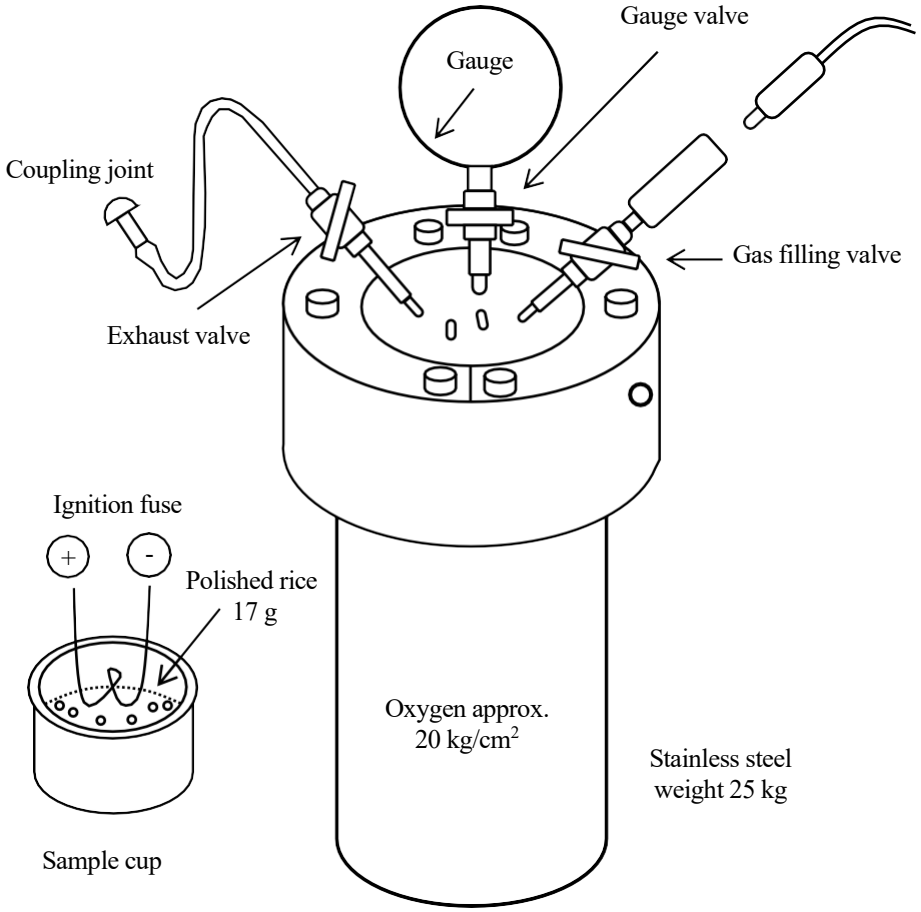


Figure 4-1 System for rapid sample combustion (commercially available)



Figure 4-2 Photographs of the rapid sample combustion system

(left: before assembly; right: after assembly)

Chapter 5 Measurement

Measurements are performed using a liquid scintillation counter. A blank sample is prepared from marble[*34], and a standard sample for determining counting efficiency (hereinafter referred to as the "standard sample") is prepared from NIST oxalic acid[*35] (see Sections 5.1 and 5.2).

Two methods are adopted for the preparation and measurement of test samples:

(1) a method in which benzene is synthesized, mixed with a scintillator solution, and then measured (hereinafter referred to as the "benzene synthesis method"); and (2) a method in which CO_2 is absorbed by a CO_2 absorbent and then measured (hereinafter referred to as the "CO_2 absorption method") (see Sections 5.3 and 5.4).

5.1 Preparation of blank measurement samples

Calcium carbonate is prepared from marble and processed in the same manner as the test samples to obtain a blank measurement sample.

5.1.1 Equipment, instruments, and reagents

(1) Equipment

1) Drying oven

(2) Instruments

1) Erlenmeyer flask: 1 L volume
2) Introduction tube: See Figures 5-1 and 5-2
3) Gas burner
4) Filtration tool: Büchner funnel (Ø 9 cm)
5) Suction flask
6) Glass rod
7) Beaker: 3 or 5 L capacity
8) Filter paper: No. 5C (Ø 9 cm)
9) Porcelain dish
10) Aluminum laminate bag
11) Desiccator

(3) Reagents

1) Marble
2) Hydrochloric acid[*36,*37,*38]: Special grade

・ Hydrochloric acid (1+1): Mix equal parts of hydrochloric acid and pure water.

[*]34 Marble consists primarily of calcium carbonate.
[*]35 Available from NIST as a standard material at the natural ^{14}C level. For specific radioactivity of ^{14}C, see Explanation A.

3) Ammonia water[*36,*37,*38]: Special grade; mass fraction of 28.0%–30.0%

・ Ammonia water (1+1): Mix equal parts of pure water and ammonia water.

4) Calcium chloride: Special grade, anhydrous or dihydrate

5) Calcium oxide[*37]: Special grade

5.1.2 Procedure

(a) Preparation of CO_2-free ammonia water (see Figure 5-1)

(1) Boil 500 mL of pure water to remove dissolved CO_2 and transfer it to Erlenmeyer flask (A).

(2) Place approximately 10 g of powdered calcium oxide[*39] and 500 mL of ammonia water[*40] into Erlenmeyer flask (B).

(3) Connect Erlenmeyer flask (A) and Erlenmeyer flask (B) using an introduction tube.

(4) Cool Erlenmeyer flask (A) in an ice bath.

(5) Gently heat Erlenmeyer flask (B) and introduce the generated ammonia gas into Erlenmeyer flask (A) to prepare CO_2-free ammonia water.

(b) Decomposition of marble and preparation of calcium carbonate for reagent blanks (see Figure 5-2)

(1) Crush the marble into suitable pieces and place them in an empty Erlenmeyer flask (C).

(2) Add hydrochloric acid (1+1) to Erlenmeyer flask (C) to generate CO_2.

(3) After the air inside Erlenmeyer flask (C) has been displaced by the generated CO_2, attach an introduction tube to the flask.

(4) Connect the other end of the introduction tube to Erlenmeyer flask (A) containing the CO_2-free ammonia water prepared in step (a). Ensure that the tip of the introduction tube is immersed in the ammonia water so that the CO_2 is absorbed into the solution[*41].

(5) After completion of the reaction, transfer the absorption solution to a beaker and heat it. While stirring, gradually add calcium chloride to form a calcium carbonate precipitate. The required amount of calcium chloride is approximately 9.3 g per 1 g of collected carbon.

(6) Heat and age the formed precipitate[*42]. After the precipitate has settled, add 2–3 drops of hot saturated calcium chloride solution to the supernatant and confirm that no turbidity occurs. If turbidity is observed, the amount of calcium chloride added is insufficient; repeat step (5).

---

[*]36 Class III substances under the Ordinance on Prevention of Hazards due to Specified Chemical Substances (substances that may cause acute poisoning due to large-volume leakage): Measures must be taken to reduce exposure concentrations, such as by installing local exhaust ventilation systems.

[*]37 Hazardous substances that require labeling under the Industrial Safety and Health Act (substances that may endanger workers or cause health impairment) must be clearly labeled, accompanied by Safety Data Sheets, and subjected to risk assessments (including the implementation of risk-reduction measures). Employers are required to inform and educate workers on the handling of these substances.

[*]38 Substances subject to the Poisonous and Deleterious Substances Control Act (those posing a high risk of acute toxicity–related health hazards): Storage and display areas must be labeled as "Non-Pharmaceutical Poisonous Substances" or "Non-Pharmaceutical Deleterious Substances," and necessary measures must be taken to prevent theft, loss, leakage, and similar incidents.

[*]39 Dissolved CO_2 is removed by adding an excess amount of calcium oxide and converting it into calcium carbonate.

[*]40 Use ammonia water immediately after opening the container.

[*]41 Operate with care, as ammonia water tends to backflow.

[*]42 Note that when forming the calcium carbonate precipitate, insufficient aging may cause the precipitate to pass through No. 5C filter paper during filtration.

(7) Collect the precipitate by suction filtration using a Büchner funnel (No. 5C filter paper; measure dry tare weight) and a suction flask, and wash it with pure water.
(8) Place the filter paper in a porcelain dish, dry in an oven at 110°C for at least 4 h, After measuring the dry precipitate weight (including the filter paper), seal it in an aluminum laminate bag and store it in a desiccator.

For subsequent operations, refer to Section 5.3.1.2 when using a custom-built benzene synthesis system, Section 5.3.2.2 when using a commercially available benzene synthesis system, and Section 5.4.1.2 when using the CO_2 absorption method.

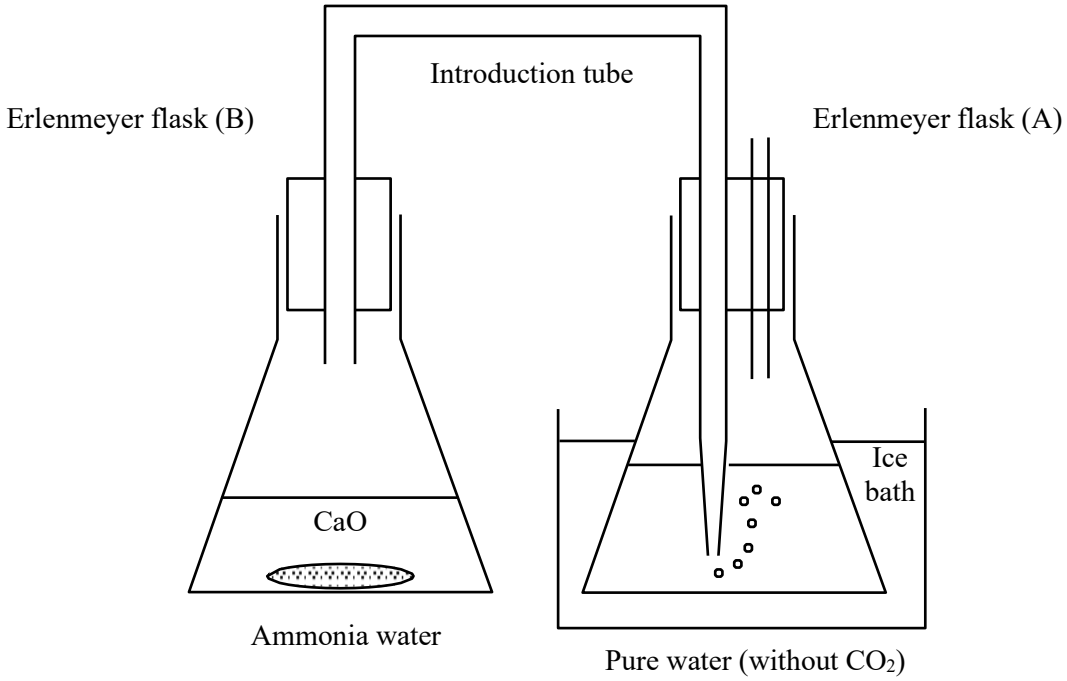


Figure 5-1 Preparation of CO_2-free ammonia water

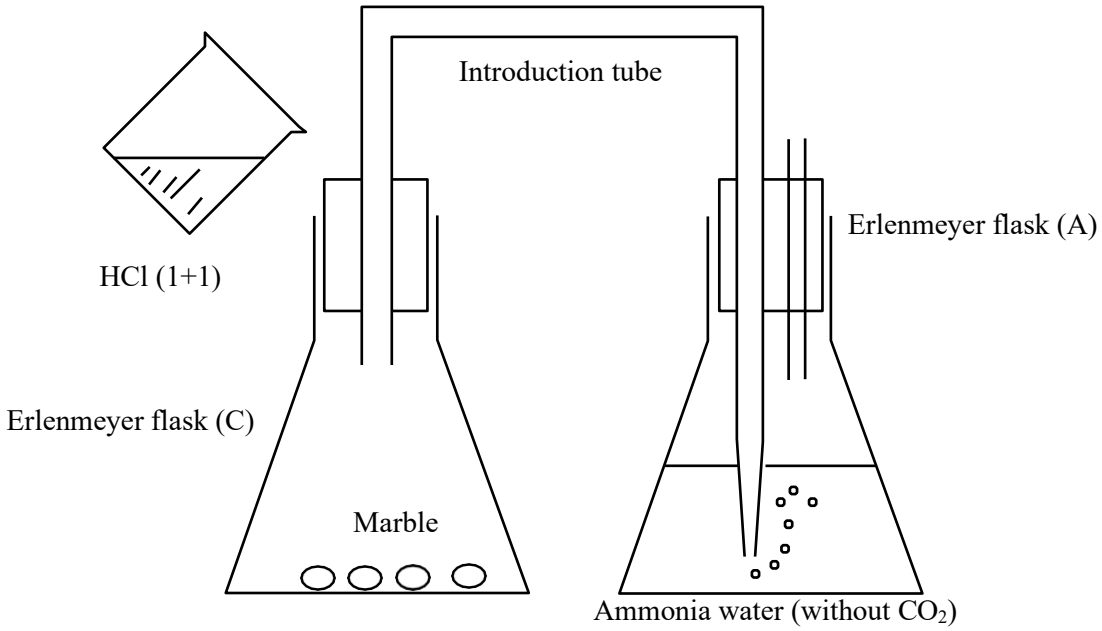


Figure 5-2 Marble decomposition and CO_2 capture system

5.2 Preparation of standard samples for counting efficiency determination

Because the specific radioactivity of ^{14}C of NIST oxalic acid is accurately determined, it is used as a calibration source for measurement instruments.

To prepare the calibration source, the oxalic acid is decomposed either by wet decomposition using the system shown in Figure 5-3 or by dry decomposition in an oxygen stream using the combustion system shown in Figure 5-4. The resulting CO_2 is collected in ammonia water. Calcium chloride is then added to this solution to form calcium carbonate. A fixed amount of the calcium carbonate is weighed and subjected to the same processing as the measurement samples to prepare the standard sample.

In the CO_2 absorption method, the counting efficiency of the sample tends to decrease continuously immediately after sample preparation; therefore, a standard sample should be prepared for each analysis[*43].

In the benzene synthesis method, the measurement sample itself (benzene) exhibits excellent scintillation properties and high purity, and no differences are observed in the shape of the scintillation spectrum among measurement samples. Therefore, once the measurement conditions are established, the counting efficiency remains stable. For this reason, it is unnecessary to prepare a standard sample from NIST oxalic acid for every analysis; it is sufficient to prepare one only for periodic checks of counting efficiency.

5.2.1 Wet decomposition method

The wet decomposition system for oxalic acid is shown in Figure 5-3.

5.2.1.1 Equipment, instruments, and reagents

(1) Equipment

1) Wet decomposition system: See Figure 5-3

(2) Instruments

1) Air pump: Suction rate of approximately 100 mL/min
2) Woulff gas washing bottles: Capacity of 250 mL
3) Glass filter gas washing bottle: Capacity of 500 mL (a Woulff gas washing bottle may also be used)
4) Three-neck round-bottom flask: Capacity of 500 mL
5) Separatory funnel: Capacity of 300 mL
6) Sampling bag[*44]: Capacity of 5 L, aluminum-laminated
7) Silicone resin tubing
8) Stirrer

[*43] This does not apply if it can be confirmed that the counting efficiency does not decrease.
[*44] Sampling bags are suitable for sampling inorganic gases because they do not allow permeation or adsorption of inorganic gases.

9) Filtration tool: Büchner funnel (Ø 9 cm)

10) Suction flask

11) Glass rod

12) Filter paper: No. 5C (Ø 9 cm)

13) Porcelain dish

14) Nitrogen gas: Purity of 99.999%.

15) Aluminum laminate bag

16) Desiccator

(3) Reagents

1) NIST oxalic acid ($H_2C_2O_4 \cdot 2H_2O$)

2) Potassium permanganate[*37,*45,*46]: Special grade reagent

· Potassium permanganate solution: Dissolve 3.5 g of potassium permanganate in 250 mL of pure (degassed) water.

3) Sulfuric acid[*36, *37, *47]: Special grade

· Potassium permanganate–sulfuric acid solution: Dissolve 12 g of potassium permanganate in 260 mL of pure (degassed) water, then gradually add 40 mL of sulfuric acid.

4) Silver nitrate[*37, *47,*48] : Special grade

· Silver nitrate solution: Dissolve 10 g of silver nitrate in 250 mL of pure (degassed) water.

5) Potassium dichromate[*37, *45,*46, *47,*49] : Special grade

· Potassium dichromate–sulfuric acid solution: Dissolve 5 g of potassium dichromate in 210 mL of pure (degassed) water, then add 40 mL of sulfuric acid.

6) Ammonia water[*36,*37,*38]: Special grade; mass fraction of 28.0–30.0%

· Ammonia water (1+1): Mix equal parts of pure water and ammonia water.

7) Calcium chloride: Special grade, anhydrous or dihydrate

8) Nitrogen gas: Purity of 99.999%.

5.2.1.2 Procedure

(1) Weigh 16 g of NIST oxalic acid into a three-neck round-bottom flask.

(2) Add 250 mL of potassium permanganate solution to Woulff gas washing bottle (1).

(3) Add 250 mL of silver nitrate solution to Woulff gas washing bottle (2).

(4) Add 250 mL of potassium dichromate–sulfuric acid solution to Woulff gas washing bottle (3).

---

*45 Class II substances under the Ordinance on Prevention of Hazards due to Specified Chemical Substances (substances that cause chronic or delayed health effects such as cancer): measures must be taken to control sources of gas, vapor, or dust emissions, such as installing local exhaust ventilation systems.

*46 Classified as a Class I hazardous material (oxidizing solid) under the Fire Service Act. Care should be taken to avoid contact with strong acids, to avoid storage with combustible materials, and to avoid heating, impact, and friction.

*47 Substances subject to the Poisonous and Deleterious Substances Control Act (those posing a high risk of acute toxicity-related health hazards): storage and display areas must be labeled as "Non-Pharmaceutical Poisonous Substances" or "Non-Pharmaceutical Deleterious Substances," and necessary measures must be taken to prevent theft, loss, leakage, and similar incidents.

*48 Classified as a Class I hazardous material (oxidizing solid) under the Fire Service Act. Care should be taken to avoid contact with strong acids, to avoid storage with combustible materials, and to avoid heating, impact, and friction.

*49 Dichromate is sometimes written as bichromate; both terms refer to the same substance.

(5) Add 300 mL of potassium permanganate–sulfuric acid solution to the separatory funnel.
(6) Add 400 mL each of ammonia water (1+1) to glass filter gas washing bottles (4) and (5).
(7) Assemble the system as shown in Figure 5-3.
(8) Purge the system with nitrogen gas from a gas cylinder to replace the air inside the system.
(9) Introduce approximately 2 L of nitrogen gas into the sampling bag.
(10) Start the air pump and draw the nitrogen gas from the sampling bag at a flow rate of approximately 100 mL/min.
(11) Gradually add the potassium permanganate–sulfuric acid solution dropwise to decompose the NIST oxalic acid. As the solution is added, the color turns brown; however, as the decomposition proceeds, the permanganate ions are consumed and the solution becomes colorless. At this point, add small additional amounts of the potassium permanganate–sulfuric acid solution.
(12) Pass the generated CO_2 sequentially through gas washing bottles (1) to (3)[*50] and collect it in the ammonia water contained in gas washing bottles (4) and (5).
(13) When decomposition is complete[*51], some of the generated CO_2 remains in the sampling bag. Introduce approximately 2 L of nitrogen gas from the nitrogen cylinder into the sampling bag, then pass the gas through gas washing bottles (1) to (3) and into the ammonia water in gas washing bottles (4) and (5). Repeat this operation several times to flush the sampling bag.
(14) Transfer the absorption solution to a beaker, heat it, and, while stirring, gradually add calcium chloride to form a calcium carbonate precipitate. The required amount of calcium chloride is approximately 9.3 g per 1 g of collected carbon.
(15) Heat-age the precipitate[*52]. After the precipitate has settled, add 2–3 drops of hot, saturated calcium chloride solution to the supernatant and confirm that no turbidity appears. If turbidity occurs, the amount of calcium chloride added is insufficient; therefore, repeat step (14).
(16) Filter the precipitate under suction using a Büchner funnel fitted with No. 5C filter paper (record the dry tare weight) and a suction flask, and then wash the precipitate with pure water.
(17) Place the filter paper in a porcelain dish, dry in an oven at 110°C for at least 4 h, After measuring the dry weight of the precipitate (including the filter paper), seal it in an aluminum laminate bag and store it in a desiccator.

For subsequent operations, refer to Section 5.3.1.2 when using a custom-built benzene synthesis system or to Section 5.4.1.2 when using the CO_2 absorption method.

[*50] Formic acid may be produced as a decomposition byproduct. When formic acid is decomposed with sulfuric acid, carbon monoxide is generated. This operation is performed to oxidize carbon monoxide to CO_2.
[*51] The point at which the brown coloration of potassium permanganate no longer disappears is used as an indicator that the reaction has completed. However, to ensure complete decomposition of oxalic acid, it is recommended to add the entire volume of the potassium permanganate–sulfuric acid solution.
[*52] When forming the calcium carbonate precipitate, insufficient aging may allow the precipitate to pass through No. 5C filter paper during filtration.

5.2.2 Wet decomposition method using a commercially available benzene synthesis system

5.2.2.1 Equipment, instruments, and reagents

(1) Equipment

1) Commercial benzene synthesis system (Figure 5-8)

(2) Instruments

1) Balance: minimum readability 0.01 g

(3) Reagents

1) NIST oxalic acid ($H_2C_2O_4 \cdot 2H_2O$)
2) Potassium permanganate[*37,*45,*46]: Special grade
3) Sulfuric acid[*36, *37, *47]: Special grade

- Potassium permanganate–sulfuric acid solution: Dissolve 12 g of potassium permanganate in 260 mL of pure (degassed) water, then gradually add 40 mL of sulfuric acid.
- Dry ice–alcohol coolant
- Liquid nitrogen

5.2.2.2 Procedure

This section describes the preparation of standard samples using NIST oxalic acid with a commercial benzene synthesis system. When using a custom-made benzene synthesis system, benzene may be synthesized from calcium carbonate samples obtained by wet or dry decomposition of NIST oxalic acid.

NIST oxalic acid is decomposed using an acid decomposition flask to generate CO_2, which is then collected. Because the specific radioactivity of ^{14}C of NIST oxalic acid is precisely determined, it is used as a calibration source for measurement instruments. The entire sequence of operations, from benzene synthesis to measurement, must be conducted carefully to prevent cross-contamination.

(1) Place approximately 24 g of NIST oxalic acid into the acid decomposition flask, add 225 mL of pure water and a stirring bar, and dissolve while stirring.
(2) While stirring, add 15 mL of sulfuric acid to the acid decomposition flask.
(3) Place 18 g of potassium permanganate into a 500 mL conical beaker, add 300 mL of pure water, then slowly add 7.5 mL of sulfuric acid while stirring thoroughly.
(4) Transfer the prepared potassium permanganate–sulfuric acid solution into the separatory funnel for the acid decomposition flask.
(5) Assemble the acid decomposition flask and separatory funnel, and connect them to Joint-1 of the benzene synthesis system (see Figure 5-8).
(6) Cool trap T-1 with a dry ice–alcohol coolant, and cool traps T-2 and T-3 with liquid nitrogen.
(7) To evacuate air from the acid decomposition flask, open valve V-17, set valve V-14 to the “red” direction, open valve V-1, and evacuate until gauge G-1 reaches −25 inHg. Then

close valve V-1.

(8) After approximately 1–2 min, set valve V-14 to the "blue" direction and close valve V-17.

(9) Turn on the stirrer and open valve V-1 while stirring the oxalic acid solution.

(10) Add the potassium permanganate–sulfuric acid solution dropwise to decompose the oxalic acid and generate CO_2. When gauge G-1 reaches approximately −15 inHg, open valves V-2, V-3, V-4, V-5, V-6, and V-8 to collect CO_2.

(11) When the pressure on gauge G-1 drops to −20 inHg, close valve V-2 and wait until the pressure rises to −10 to −5 inHg.

(12) When the pressure rises to −10 to −5 inHg, open valve V-2 to collect CO_2. Repeat this operation until decomposition is complete and gas generation ceases.

(13) When the solution changes from transparent to brown and CO_2 generation stops, open valves V-2 and V-9 to collect dissolved CO_2.

(14) After closing valves V-1, V-2, and V-9, remove the acid decomposition flask from the system.

(15) While monitoring pressure on gauge G-1, remove the liquid nitrogen and open valve V-9 to evacuate the system.

(16) Close valves V-5 and V-9, then sequentially open valves V-11, V-12, and V-13 to store CO_2 in the storage tank.

(17) After all CO_2 in the traps has vaporized, close valves V-12 and V-13. Cool the microtrap with liquid nitrogen and collect all remaining CO_2 from traps T-1 and T-2.

(18) Close valve V-11, open valves V-12 and V-13, remove the liquid nitrogen from the microtrap, and transfer the contents to the storage tank.

For subsequent operations, see Section 5.3.2.2, Procedure (a), Sample decomposition.

5.2.3 Dry decomposition method

The dry decomposition system for oxalic acid is shown in Figure 5-4.

5.2.3.1 Equipment, instruments, and reagents

(1) Equipment

1) Sample combustion system: movable tubular furnace (see Figure 5-4)

(2) Instruments

1) Quartz double-tube combustion tube: outer tube, 900 mm length × Ø 40 mm; inner tube, 400 mm length × Ø 30 mm
2) Quartz wool
3) Woulff gas washing bottles: Capacity of 500 mL
4) Glass filter gas washing bottle: Capacity of 250 mL
5) Silicone resin tubing

(3) Reagents

1) NIST oxalic acid ($H_2C_2O_4 \cdot 2H_2O$)
2) Copper oxide[*37]: Wire form
3) Ammonia water[*36,*37,*47]: Special grade; mass fraction of 28.0%–30.0%

· Ammonia water (1+1): Mix equal parts of pure water and ammonia water

4) Oxygen gas: Purity of ≥99.7%
5) Nitrogen gas: Purity of 99.999%.

5.2.3.2 Procedure

(1) Weigh 12 g of NIST oxalic acid into the inner tube of the quartz double-tube combustion tube, and pack quartz wool at both ends. Distribute the oxalic acid evenly within the inner tube.
(2) Pack copper oxide into the left end of the outer tube of the quartz double-tube combustion tube, and pack quartz wool at both ends.
(3) Fill two Woulff gas washing bottles with 500 mL each of ammonia water (1+1).
(4) Assemble the system as shown in Figure 5-4.
(5) Supply oxygen gas to the outer tube at a flow rate of 50 mL/min.
(6) Supply nitrogen gas to the inner tube at a flow rate of 40 mL/min.
(7) Heat the second combustion furnace to 650°C.
(8) Supply oxygen gas to the inner tube at a flow rate of 40 mL/min.
(9) Place the first combustion furnace at the right end of the combustion tube and raise its temperature to 400°C.
(10) Move the first combustion furnace 1 cm to the left every 15 min to combust the oxalic acid. During this process, CO_2 is produced as the main product, and carbon monoxide is generated as a by-product. The carbon monoxide is completely oxidized to CO_2 by the combustion promoter (copper oxide), and the resulting CO_2 is captured in the ammonia solution.
(11) After decomposition is complete, stop the supply of oxygen and nitrogen gases.
(12) Transfer the ammonia water (1+1) from the Woulff gas washing bottles to a beaker, heat it, and react it with calcium chloride to form calcium carbonate.
(13) After filtering and drying the calcium carbonate precipitate, measure its weight and calculate the recovery (typically ≥95%). Seal the sample in an aluminum-laminated bag and store it in a desiccator.

For subsequent operations, refer to Section 5.3.1.2 when using a custom-built benzene synthesis system, or Section 5.4.1.2 when using the CO_2 absorption method.

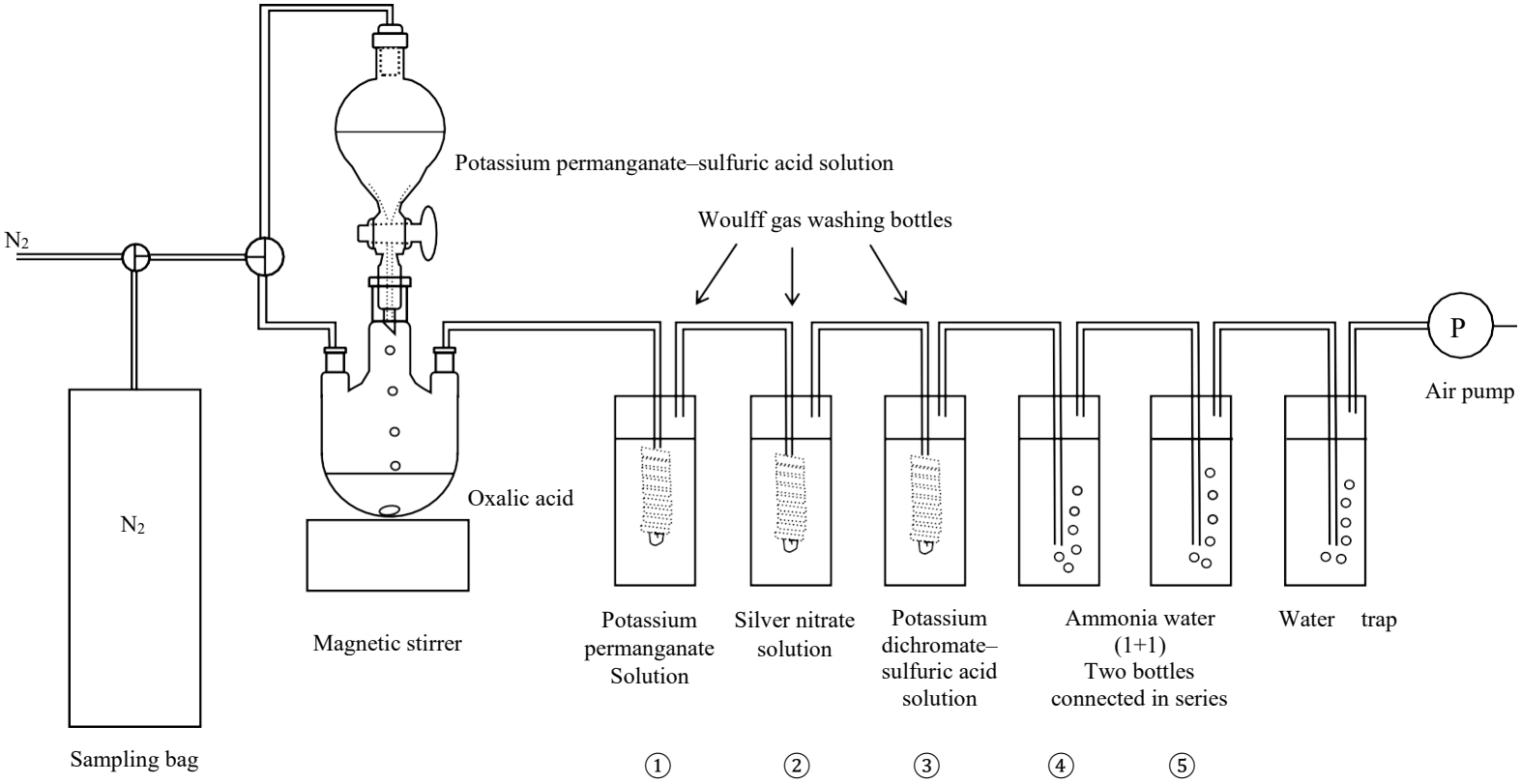


Figure 5-3 Wet decomposition system for oxalic acid

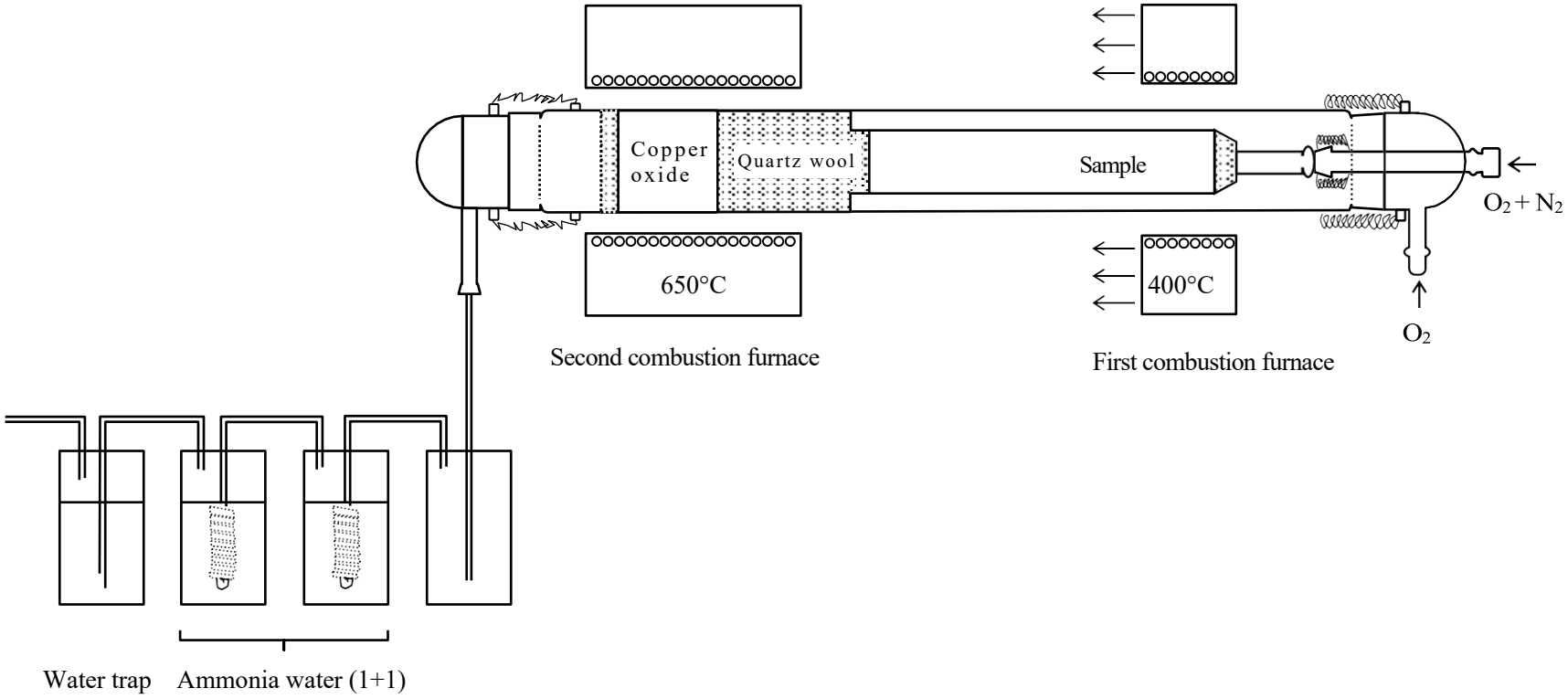


Figure 5-4 Dry decomposition system for oxalic acid

5.3 Liquid scintillation counting using the benzene synthesis method

This method involves synthesizing benzene, which has the highest carbon content per unit mass, from CO_2, mixing it with a scintillator solution, and then performing the measurement.

CO_2 is generated from calcium carbonate prepared using the methods described in Chapters 1, 2, 3, and 4. The CO_2 is then converted to benzene, which is mixed with a scintillator to prepare the measurement sample. The general steps involved in synthesizing benzene are outlined below (see Figure 5-5).

(1) Decomposition of carbonate: $CaCO_3 + 2HClO_4 \rightarrow CO_2 + Ca(ClO_4)_2 + H_2O$

CO_2 is generated by acid decomposition.

(2) Formation of lithium carbide: $2CO_2 + 10Li \rightarrow Li_2C_2 + 4Li_2O$

Lithium carbide is produced by the reaction of CO_2 with metallic lithium.

(3) Formation of acetylene: $Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH$

Acetylene gas is generated by the gradual addition of pure water.

(4) Synthesis of benzene: $3C_2H_2 \rightarrow C_6H_6$ (catalytic reaction)

Benzene is synthesized through the trimerization of acetylene.

When benzene is synthesized from calcium carbonate using a custom-built benzene synthesis system (see Figure 5-6), the total analytical time required is approximately two days per sample.

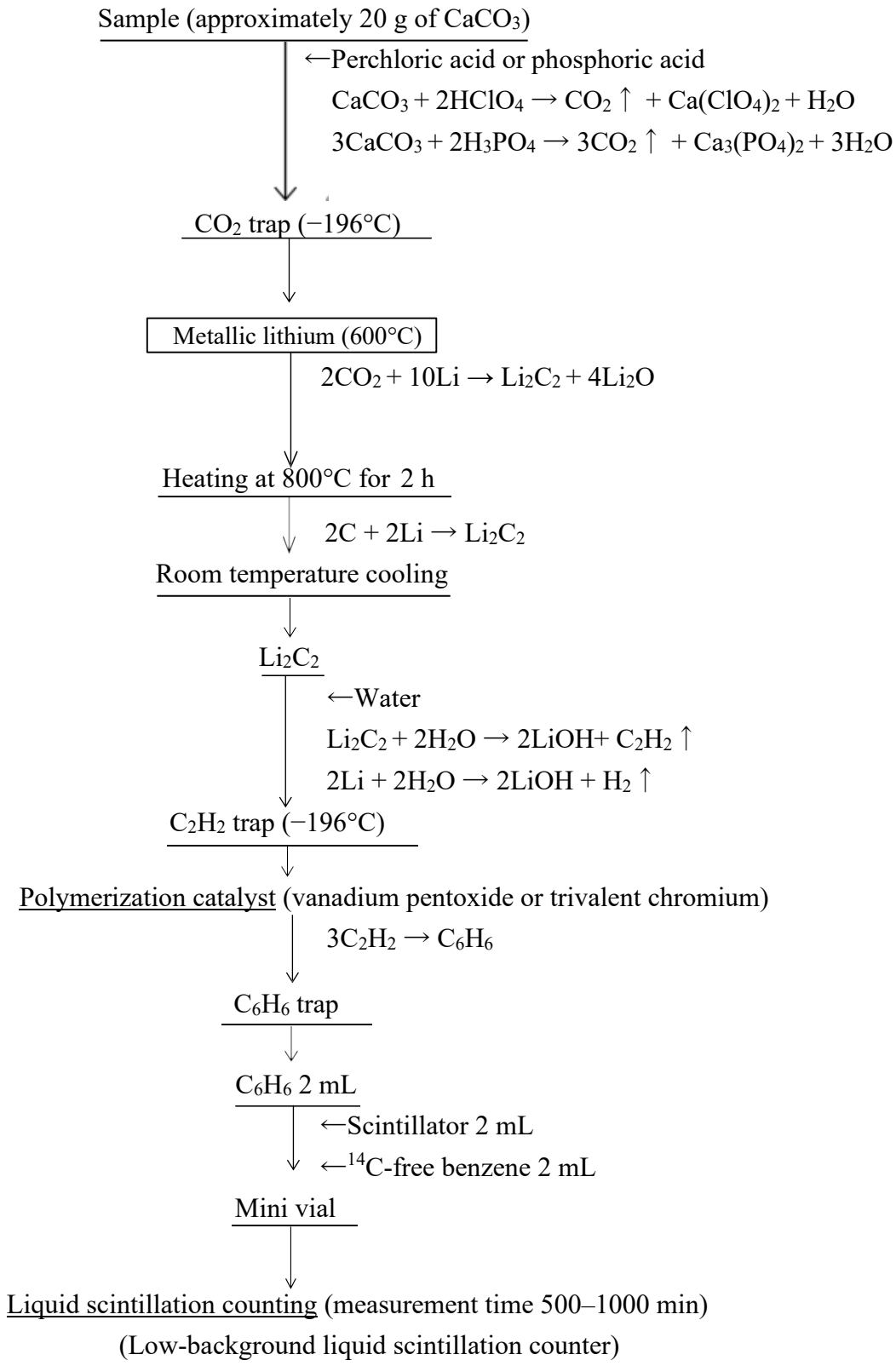


Figure 5-5 Benzene synthesis process diagram

5.3.1 Procedure when using a custom-built benzene synthesis system

5.3.1.1 Equipment, instruments, and reagents

Reagents compliant with Japanese Industrial Standards (JIS) shall be used. When no standard is specified, the highest available reagent grade shall be selected.

(1) Equipment

1) Custom-built benzene synthesis system: Figures 5-6 and 5-7
2) Electric furnace

(2) Instruments

1) Vacuum desiccator
2) Dewar flask: Capacity of 500 mL
3) Laboratory jack
4) Stirrer
5) Quartz wool
6) Vacuum grease: Free of silicone and halogens
7) Mantle heater

(3) Reagents

1) Perchloric acid[*53,*54]: Special grade; mass fraction of 60%
2) Ethanol[*54,*55]: Special grade
3) Liquid nitrogen
4) Catalyst for benzene polymerization: Vanadium pentoxide catalyst [*54,*56,*57] or trivalent chromium alumina pellets
5) Metallic lithium [*54,*58]: Wheel-shaped or rod-shaped, with purity of ≥99.8%[*59]. Metallic lithium stored in oil shall not be used due to the risk of carbon contamination.

[*53] Classified as a Class I hazardous material (oxidizing liquid) under the Fire Service Act. Precautions include preventing contact with the human body, keeping the material away from combustible substances and metals, using acid-resistant storage containers, and ensuring that it does not come into contact with water or moisture.

[*54] Hazardous substances that require labelling under the Industrial Safety and Health Act (i.e., substances that may endanger workers or cause health impairment) must be clearly labelled, accompanied by Safety Data Sheets, and subjected to risk assessments (including the implementation of risk-reduction measures). Employers are required to inform and educate workers about the proper handling of these substances.

[*55] Classified as a Class IV hazardous material (flammable liquid) under the Fire Service Act. The following precautions are required: open flames must be strictly avoided; the material shall be stored and handled below its flash point; it shall be kept separate from Category I and Category V hazardous substances; measures shall be implemented to prevent static electricity; and when transferring the material to smaller containers, they should not be filled to full capacity to prevent potential rupture due to thermal expansion.

[*56] Class II substances under the Ordinance on Prevention of Hazards due to Specified Chemical Substances (i.e., substances that cause chronic or delayed health effects, such as cancer). Measures shall be implemented to control sources of gas, vapor, or dust emissions, including the installation of local exhaust ventilation systems.

[*57] Substances subject to the Poisonous and Deleterious Substances Control Act (i.e., substances posing a high risk of acute toxicity-related health hazards). Storage and display areas must be labeled as “Non-Pharmaceutical Poisonous Substances” or “Non-Pharmaceutical Deleterious Substances,” and appropriate measures must be taken to prevent theft, loss, leakage, and similar incidents.

[*58] Classified as a Class III hazardous material (spontaneously combustible and water-reactive substances) under the Fire Service Act. Avoid contact with air, water, moisture, flames, sparks, or other high-temperature objects. Store under a protective liquid or in an inert gas, such as argon, and subdivide for storage as necessary.

[*59] Metallic lithium is normally stored in a vacuum desiccator; however, long-term storage is difficult. Commercially available lithium sealed in aluminum bags under argon gas is recommended, and it is preferable to use one package per analytical batch.

5.3.1.2 Procedure

Due to the length of the process, it may be divided into three stages: Day 1: up to step (g), formation of lithium carbide; Day 2: up to step (l), benzene synthesis by acetylene polymerization; and Day 3: step (m), baking out of benzene. When dividing the process in this manner, after completing all work for the day, open all valves except valves X, Y, C, J, and A, and evacuate the system under vacuum. After evacuation, close all valves except valve O, and then perform step (o), stopping the vacuum pump. On the following day, install trap N and, after performing step (a), leak checking and evacuation of the vacuum line, resume the procedure from the step following the previous day's work.

(a) Leak check and evacuation of the vacuum line

(1) Cool liquid nitrogen trap N in the vacuum line with liquid nitrogen[*60].

(2) Start the vacuum pump (oil rotary pump).

(3) Confirm that all valves in the vacuum line are closed, then open valve O. To check the vacuum level in the line (presence or absence of leaks), open valves beginning with those closest to the pump.

(4) Open valves M, Q, and R in this order.

(5) Open valve B and evacuate until the Pirani vacuum gauge indicates approximately ≤1 Pa [*61,*62].

(6) Open valve L and evacuate until the Pirani vacuum gauge indicates approximately ≤1 Pa.

(7) Open valve I and evacuate until the Pirani vacuum gauge indicates approximately ≤1 Pa.

(8) Open valve H and evacuate until the Pirani vacuum gauge indicates approximately ≤1 Pa.

(9) Open valves S and T of trap L and confirm the vacuum level in the same manner.

(10) Open valves V and W of trap I and confirm the vacuum level in the same manner.

(11) Open each valve of traps D and E and confirm the vacuum level in the same manner. The weight of trap D shall be measured in advance.

(12) Open valve P of the gas reservoir (6 L) and confirm the vacuum level in the same manner.

(13) Open all remaining valves in the lower line, except valves X, Y, C, J, A, and P, and evacuate until the vacuum level reaches approximately ≤1 Pa.

(14) Open valve F and adjust the manometer reading (a digital type is convenient) to 0.0 kPa, displayed to one decimal place, using the zero-adjustment knob.

(15) Temporarily close all valves in the vacuum line except valve 0. Close the valves sequentially, starting with those farthest from the vacuum pump.

(b) Preparation of the coolant

(1) Prepare a liquid nitrogen–ethanol coolant (−70°C or lower) in a Dewar flask.

---

[*]60 Trap N is installed for two purposes: to prevent oil used in vacuum pumps from spreading into the vacuum line and to prevent moisture in the line from entering the pump. During operation, care shall be taken to ensure that trap N is always cooled with a sufficient amount of liquid nitrogen.

[*]61 The pressure unit most commonly used in analytical methods is Torr (mmHg). The relationship with Pa (pascal), which is used in the International System of Units (SI), is shown below:
1 Torr = 1 mmHg = 1.333×10^2 Pa

[*]62 The indicated vacuum level is a reference value achieved after sufficient evacuation.

(c) Activation of the catalyst

(1) Activate the polymerization catalyst [*63, *64].

Place 120 g of vanadium pentoxide catalyst in a porcelain dish and heat it in an electric furnace at 500°C for at least 4 h. The furnace should be of a nonsealed type and equipped with ventilation openings so that the air (oxygen) inside the furnace is continuously exchanged. If a sealed furnace is used, heating should be performed with the sample access door slightly open.

(d) Decomposition of the sample (calcium carbonate)

(1) Place approximately 20 g of the sample (calcium carbonate)[*65] into the reaction vessel (300–500 mL) of the sample decomposition system. At this stage, it is preferable to place the sample at the bottom of the vessel and avoid adhesion to the vessel walls as much as possible.

(2) Place a stir bar into the vessel, then add approximately 10 mL of degassed water to thoroughly moisten the sample. This step is necessary to prevent splashing of the sample onto the vessel walls when perchloric acid is added dropwise.

(3) Place the required amount[*66] of perchloric acid[*67] for decomposition into the dropping funnel.

(4) Apply vacuum grease to the joint of the upper cock of the dropping funnel and confirm that there is no leakage.

(5) Set the stirrer unit beneath the reaction vessel.

(6) Pack quartz wool (or lightly rolled sealing tape) into the joint between valve J and the reaction vessel, and set the reaction vessel in the designated position on the vacuum line[*68].

(7) Set the dropping funnel into the reaction vessel.

(8) After confirming that all valves on the vacuum line are closed, open valves M, L, and J, and evacuate the reaction vessel for approximately 3 min.

(9) Close valve L[*69].

(10) Cool trap K with liquid nitrogen.

(11) Open the cock of the dropping funnel and add perchloric acid dropwise to decompose the sample. The gases generated at this stage are CO_2 and water vapor.

(12) Confirm that CO_2 is trapped in trap K.

(13) After the decomposition reaction subsides, add perchloric acid dropwise again. After adding a certain amount, repeat the same operation while rotating the stirrer, and completely decompose the entire sample.

---

*63 The catalyst used is either activated vanadium pentoxide supported on an alumina carrier or a commercially available catalyst that is activated immediately before use.

*64 At this stage, the catalyst color changes from dark brown to yellow–green. Heating is performed to remove impurities and activate the catalyst. In particular, adsorption of moisture on the catalyst reduces reaction efficiency.

*65 To maintain negative pressure within the system and prevent sample loss, the sample amount should be adjusted so that the pressure in the gas reservoir does not exceed atmospheric pressure when the gas diffuses into it.

*66 CO_2 may be generated using perchloric acid or phosphoric acid. If the acid is added too rapidly, foaming may occur, filling the reaction vessel with sample powder and causing overflow. Therefore, the acid should be added slowly while observing the reaction, gently shaking the vessel as needed to ensure uniform distribution.

*67 To decompose 25 g of calcium carbonate, 55 mL of 60% perchloric acid is sufficient.

*68 This step prevents perchloric acid foam from splashing into the vacuum line.

*69 Keep this valve closed during the decomposition reaction. Opening the valve will result in CO_2 loss.

(14) Close valve J after the decomposition is complete.
(15) Open the upper cock of the dropping funnel to return the reaction vessel to atmospheric pressure.
(16) Remove the reaction vessel, wash it thoroughly, and dry it.

(e) Purification of CO_2

(1) Open valves B, F, S, Q, R, and E, and evacuate the section from trap L through the upper line to trap E until the vacuum level reaches ≤1 Pa.
(2) Cool trap L with a liquid nitrogen–ethanol coolant (for moisture removal).
(3) Close the valves opened in step (1), except for valves B and F (i.e., close S, Q, R, and E)[*70].
(4) Slightly lift the Dewar flask containing liquid nitrogen set on trap K (to raise the liquid nitrogen level), slightly open valve L, and evacuate[*71].
(5) Close valves B[*72], L, and M.
(6) Cool trap E with liquid nitrogen.
(7) Open valves T, S, Q, R, and E.
(8) Gently warm trap K with cool air from a dryer to gradually vaporize the CO_2.
(9) As the CO_2 vaporizes, the pressure rises to approximately 5 kPa. At this stage, confirm that CO_2 adheres to the inner surface of trap E, forming a white frost. If no adhesion is observed, the pressure inside the line may rise abnormally[*73]. In such cases, cool trap K again with liquid nitrogen and recheck the valves and connections.
(10) Confirm that water is trapped as ice on the inner wall of trap L.
(11) As the CO_2 in trap K vaporizes, the digital manometer reading, which had been increasing, begins to decrease. At this point, CO_2 is transferring to trap E. Although a small amount of moisture may remain in the inner tube of trap K, do not continue heating forcibly.
(12) Close valves S and T, and remove the liquid nitrogen–ethanol coolant.
(13) Continue collecting CO_2 in trap E using liquid nitrogen until the vacuum level stabilizes, ensuring that all CO_2 is captured in trap E.
(14) Close valves E[*74], R, and Q.

(f) Measurement of CO_2 recovery rate (to determine the recovery rate, perform the following operations)

Measurement of the volume of system A (once determined, benzene synthesis from the sample does not need to be performed for each measurement)

(1) Accurately determine the volume of trap E. After measuring the tare weight of trap E, fill it

---

[*]70 Valves B and F should remain open to allow continuous pressure monitoring.
[*]71 Any gas that does not solidify upon cooling with liquid nitrogen is not CO_2 and should be removed as an impurity by evacuation.
[*]72 Close valve B at this stage to prevent the pressure of vaporized CO_2 from exceeding the measurement range of the Pirani vacuum gauge, which could damage the instrument. From this step onward, pressure monitoring is performed using the digital manometer; therefore, valve F must remain open at all times.
[*]73 Heating must be carried out while continuously monitoring the digital manometer. If pressure continues to rise, CO_2 may not be captured in trap E due to a malfunction. Because rupture risk increases when pressure exceeds atmospheric pressure, heating should be stopped and trap K cooled with liquid nitrogen if the pressure exceeds 30 kPa.
[*]74 If the collected CO_2 vaporizes, the internal pressure in trap E increases, posing a rupture risk. Continue cooling with liquid nitrogen.

with pure water and measure the weight. Calculate the internal volume by assuming that 1 g of water corresponds to 1 mL (e.g., 188 g = 188 mL).

(2) Fill the sampling bag to be used with nitrogen gas and connect it to valve A.

(3) Evacuate the vacuum line sufficiently and confirm that the digital manometer indicates 0.0 kPa.

(4) Close all valves except valve 0.

(5) Open valves E, R, Q, and F (digital manometer).

(6) Slowly open valve A and allow the nitrogen gas in the sampling bag to diffuse through the upper line into trap E. Record the digital manometer reading (differential pressure) at this stage (e.g. 101 kPa).

(7) Close valves A and E.

(8) Open valve M and evacuate the upper line again. Confirm that the digital manometer reading returns to 0.0 kPa.

(9) Close valve Q and open valve P.

(10) Open valve E and allow the nitrogen gas to diffuse into the gas reservoir. Record the digital manometer reading at this stage (e.g. 2.79 kPa).

(11) Using Boyle's law (pressure × volume = constant), calculate the volume of the section into which the nitrogen gas has diffused (from trap E to gas reservoir P).
Example: 188 mL × 10^{-3} × 101 kPa / 2.79 kPa ≈ 6.81 L.

B Calculation of CO_2 yield

(1) Confirm that valves M, H, and Q are closed.

(2) Open valves R and P.

(3) Close valve B, open valve F, and confirm that the digital manometer reading is 0.0 kPa. Open valve E and remove the liquid-nitrogen trap from trap E.

(4) Warm trap E using cool air from a dryer[*75] and allow the CO_2 to diffuse from valve H through the upper line into the section of known volume extending to the gas reservoir and valve Q.

(5) Check the digital manometer reading. The reading, initially 0.0 kPa, should gradually increase as the CO_2 vaporizes (e.g., approximately 7.23 kPa).

(6) Confirm that no residue remains in trap E. If water droplets are present at the bottom of trap E, moisture removal is insufficient. In this case, repeat the CO_2 purification step (e).

(7) Cool trap E with cool air from a dryer to prevent an increase in internal pressure due to thermal expansion.

(8) Measure the room temperature using a thermometer (e.g. 24.3°C)

(9) Confirm the final digital manometer reading (e.g., approximately 7.23 kPa).

(10) Calculate the CO_2 yield using the ideal gas equation (PV = nRT), where the gas constant R = 8.31 × 10^3 Pa·L/mol/K.

(11) Calculate the carbon recovery rate (typically ≥90%) for the conversion of calcium carbonate to CO_2.

[*75] Warm air may also be used; however, extreme caution is required to avoid a rapid pressure increase caused by sudden vaporization of CO_2. Rapid heating may cause dry-ice fragments to scatter and clog narrow tubing sections. Depending on the blockage location, localized pressure increases may occur. Proceed while continuously monitoring the system.

(12) Cool trap E again with liquid nitrogen and collect the CO_2. Confirm that the digital manometer reading approaches the initial value (0.0 kPa)[*76].

(g) Production of lithium carbide

After placing metallic lithium into a pressure-resistant metal vessel and evacuating the air, heat the bottom of the vessel so that the lithium gradually reacts with CO_2 to form lithium carbide.

(1) Wear laboratory gloves (e.g., polyethylene disposable gloves).
(2) Remove metallic lithium (wheel-shaped or rod-shaped) from the vacuum desiccator.
(3) Cut the required amount of lithium based on the reaction stoichiometry (e.g., 3.8 g of lithium for 10 g of calcium carbonate) and place it at the bottom of the low-pressure reaction vessel. Use approximately 10% excess lithium.
(4) Close the lid of the low-pressure reaction vessel, connect it to the vacuum line, and attach a pressure gauge.
(5) Close valve E and continue cooling trap E with liquid nitrogen.
(6) Close valve P.
(7) Open valves B, F, M, Q, R, Y, and X in that order and evacuate the reaction vessel from the upper line. Evacuation should be performed gradually, starting from the side closer to the vacuum pump.
(8) Allow the vacuum to improve; this process typically requires 30 min–1 h.
(9) Confirm that the Pirani vacuum gauge reading is ≤8 Pa.
(10) Circulate cooling water through the low-pressure reaction vessel.
(11) Heat the bottom of the vessel using a gas burner[*77].
(12) Confirm that the lithium has melted[*78]. Gently shake the vessel to distribute the molten lithium evenly over the bottom surface.
(13) Close valve R.
(14) Confirm that the Pirani gauge reading is ≤8 Pa, then close valve B. Keep valve F (digital manometer) open.
(15) Open valve E, remove the liquid nitrogen from trap E, and warm trap E using cool or warm air from a dryer[*79] to vaporize the CO_2 and allow it to react with the molten lithium. The lithium surface will gradually turn black[*80].

---

[*]76 This step requires approximately 30 min.

[*]77 When heating begins, degassing from the surface of the metallic lithium temporarily worsens the vacuum. Because the reaction is exothermic, maintain the temperature at approximately 600°C during the initial stage while observing the vessel bottom as it becomes red-hot. Once the reaction proceeds spontaneously, continue introducing CO_2 gradually while monitoring the internal pressure of the vessel.

[*]78 At the moment of melting, the pressure reaches a maximum (i.e., the vacuum is at its worst), after which it rapidly decreases as the vacuum recovers to approximately 1.33 Pa. Avoid overheating the reaction vessel, as excessive heating may vaporize lithium and damage the glass window at the top of the vessel.

[*]79 When heating with warm air, operate with extreme caution to prevent a rapid pressure increase caused by sudden vaporization of CO_2. With either cool or warm air, dry-ice fragments detaching from the wall of trap E may scatter and clog narrow tubing sections. Depending on the blockage location, local pressure may increase; therefore, proceed while carefully monitoring the digital manometer.

[*]80 After introducing all the CO_2, heat strongly at approximately 800°C for at least 30 min to complete the reaction. After the formation reaction, cool the bottom of the reaction vessel with water to room temperature. Lithium carbide (Li_2C_2) can be produced with a yield of ≥95%.

Perform steps (12)–(15) as quickly as possible.

(16) Confirm that the digital manometer reading gradually increases[*81].

(17) Wait until the digital manometer reading reaches approximately 0.0 kPa[*82], indicating completion of the reaction.

(18) Close valve X.

(19) Close valve Y.

(20) Continue heating the reaction vessel at approximately 800°C for at least 1 h[*83]. Confirm that the lithium surface has turned gray, indicating progress of lithium carbide formation.

(21) Stop heating.

(22) Cool the vessel using cool air from a dryer until it reaches room temperature.

(23) Open all valves except X, Y, C, J, A, and P, and evacuate the system.

(24) Open valve P[*84] and evacuate the connected reservoir.

(25) Close all valves after evacuation is complete.

(h) Preparation of the catalyst

(1) Close all valves in the vacuum line.

(2) Transfer approximately 120 g of catalyst, previously heated at 500°C in an electric furnace, into catalyst column C while still hot. The catalyst should appear yellow–green.

(3) Connect catalyst column C to the vacuum line.

(4) Slowly open valves M, Q, R, F, and C in that order and evacuate the column from the upper line.

(5) After confirming sufficient vacuum using the digital manometer, open valve B and continue evacuation until the Pirani gauge reading is ≤0.667 Pa.

(6) Close valve C.

(7) Cool catalyst column C in ice water.

(i) Production of acetylene

(1) Cool the low-pressure reaction vessel containing lithium carbide in ice water.

(2) If closed, open valves M, S, T, V, W, H, and F, and evacuate the system.

(3) Close valves Q and R if open (the upper line is not used.)

(4) Cool traps I and G using a liquid nitrogen–ethanol coolant for moisture removal.

(5) Cool traps K and L with liquid nitrogen for acetylene collection.

(6) Install the water tank in the reaction vessel and add 1–1.5 L of degassed water[*85].

[*81] Initially, vaporization of CO_2 causes the pressure to rise to approximately 40–55 kPa; however, as the reaction proceeds, the pressure decreases.

[*82] The indicated pressure may not return to 0.0 kPa due to heating. If the pressure stabilizes at a constant value, the reaction is considered complete.

[*83] Evacuation from step (23) onward may be performed in parallel with heating.

[*84] The 3 L gas reservoir connected via valve P has a large volume, and initiating evacuation immediately would require a long time. By first evacuating the other sections and sufficiently reducing the overall system pressure, then opening valve P, the total evacuation time can be shortened.

[*85] Acetylene is generated by adding pure water gradually. Use degassed water that has been boiled and cooled to remove dissolved

(7) Confirm that valves B, C, L, and I are closed.

(8) Close valve S.

(9) Open valves X and Y.

(10) Slightly open injection valve Z and gradually introduce water into the reaction vessel to generate acetylene. Confirm acetylene collection in traps K and L. Continuously monitor pressure using the digital manometer. If pressure exceeds 55 kPa, slightly open valve S; if it falls below 13 kPa, close valve S[*86].

(11) After completion, confirm that pressure does not increase when valve S is closed[*87].

(12) Close valves X and Y.

(13) Close valves H and F.

(14) Close valves V and W.

(15) After confirming that valves S and L are closed and valve T is open, remove liquid nitrogen from trap L and warm it with cool air from a dryer to transfer acetylene to trap K.

(16) Close valves S and T.

(17) Open valve L and evacuate hydrogen gas using the vacuum pump (10–15 s).

(18) Close valve L.

(19) Confirm that valves S, L, Q, P, R, B, F, H, E, and C are closed. Then, close valve M and open valves A, Y, and X to return the reaction vessel to atmospheric pressure. Remove the vessel and clean it.

(20) Close valves A, X, and Y. Open valves M, Q, and R and evacuate the upper line.

(j) Purification of acetylene

(1) Open valve S and evacuate the inside of trap L.

(2) Open valves Q, R, and E, and evacuate the line from the upper line to trap E.

(3) Cool trap L with a liquid nitrogen–ethanol coolant (for moisture removal), and cool trap E with liquid nitrogen.

(4) Close valve M and open valve F (digital manometer).

(5) Remove the liquid nitrogen from trap K and gently warm it with cool air from a dryer to transfer acetylene to trap E. As acetylene vaporizes, the pressure rises to approximately 5 kPa. Confirm that acetylene adheres to the inner wall of trap E, giving it a white, cloudy appearance. If no adhesion is observed, the pressure in the line may rise abnormally[*88]. In

---

CO_2. Ideally, tritium-free water should be used; however, because the maximum β energy of tritium (approximately 18 keV) is much lower than that of ^{14}C (156 keV), its effect on ^{14}C measurement can be neglected.

[*]86 Excess lithium reacts with water to produce hydrogen, causing a pressure increase; this hydrogen is removed by evacuation and is not collected. If the valve is opened excessively, the gas flow rate becomes too high and acetylene may be exhausted before being trapped. At low pressure, water evaporates more readily, increasing the likelihood of water vapor entering the system. Adjust the valve opening to maintain the pressure between 13 and 55 kPa. If the pressure rises rapidly and appears likely to exceed atmospheric pressure, open valve S fully and simultaneously close valve Z to release pressure and prevent rupture.

[*]87 If fine bubbles (dissolved acetylene) appear in the low-pressure reaction vessel and are followed by larger bubbles, the latter indicate water vapor. At this stage, acetylene generation can be regarded as complete. To prevent air in the water tank from entering the system, it is preferable to terminate the reaction while leaving a small amount of water in the tank.

[*]88 Perform warming while continuously monitoring the digital manometer. If the pressure exceeds atmospheric pressure, the risk of vessel rupture increases. For safety, if the pressure continues to rise beyond 20 kPa, stop heating and cool trap K with liquid nitrogen to reduce the pressure.

this case, cool trap K again with liquid nitrogen and recheck the valves and connections.

(6) After all acetylene has vaporized, confirm that a small amount of moisture adheres to the inner wall of the inlet tube of trap K[*89].

(7) As acetylene is collected in trap E, the digital manometer reading begins to decrease.

(8) Close valves S and T.

(9) When the digital manometer reading has decreased sufficiently, open valve B and wait until the Pirani vacuum gauge reading stabilizes (approximately ≤1.33 Pa).

(10) Slightly open valve M for 10–15 s to discharge hydrogen through the upper line.

(11) Close valve E[*90].

(12) Open valve M and evacuate the upper line up to just before valve E.

(k) Measurement of acetylene recovery rate (perform the following steps to determine the recovery rate)

(1) Close valve Q.

(2) Open valve P.

(3) Close valve B (Pirani vacuum gauge). Confirm that valve F (digital manometer) is open and that the reading is 0.0 mmHg.

(4) Open valve E and remove the liquid-nitrogen trap from trap E.

(5) Warm trap E with cool air from a dryer and allow acetylene to diffuse via valve H through the upper line into the section of known volume extending to the gas reservoir and valve Q.

(6) Measure the room temperature with a thermometer (e.g., 24.3°C) and record the digital manometer reading[*91].

(7) Calculate the acetylene yield using the ideal gas equation ($PV = nRT$), where $R = 8.31 \times 10^3$ Pa·L/mol/K. Calculate the recovery from carbon dioxide to acetylene (normally ≥80%).

(8) Cool trap E again with liquid nitrogen to collect acetylene.
Confirm that the digital manometer reading gradually returns to the initial value (0.0 mmHg). This step takes approximately 30 min.

(9) Open valve B, check the Pirani vacuum gauge, and continue collecting acetylene with liquid nitrogen until the reading stabilizes (approximately ≤ 1.33 Pa).

(10) Close valve E[*92].

(l) Synthesis of benzene by polymerization of acetylene

(1) Confirm that valve H is closed, then close valve R.

[*89] Confirm that the white solid acetylene has disappeared. During acetylene purification, water droplets collected simultaneously may remain on the inlet tube wall of trap K; do not mistake these droplets for acetylene

[*90] When the collected carbon dioxide vaporizes, the pressure inside Trap E increases and there is a risk of rupture. Continue cooling with liquid nitrogen.

[*91] The pressure, initially at 0.0 mmHg, gradually increases as acetylene vaporizes.
(e.g., 263.4 mmHg [35,117 Pa]).
Since conversion from CO_2 to C_2H_2 halves the number of molecules, the pressure becomes approximately one-half of that obtained when CO_2 occupies the same volume.

[*92] If the collected gas vaporizes, the internal pressure of trap E increases, creating a risk of rupture. Continue cooling with liquid nitrogen.

(2) Open valves E and C.

(3) Close valve B (Pirani vacuum gauge). If valve F (digital manometer) is not open, open it.

(4) While cooling catalyst column C with ice, remove the liquid-nitrogen trap from trap E and warm it with cool air from a dryer[*93].

(5) Confirm that the catalyst color changes to brown as acetylene vaporizes.

(6) As polymerization proceeds on the catalyst, confirm that the digital manometer reading decreases. If the pressure appears likely to exceed atmospheric pressure, cool trap E with liquid nitrogen as necessary.

(7) When the digital manometer reading reaches approximately 3–5 mmHg (400–667 Pa), cool catalyst column C with liquid nitrogen and draw all acetylene into the catalyst.

After confirming that the digital manometer indicates approximately 0.0 mmHg, open valve B.

(8) Continue cooling with liquid nitrogen until the Pirani vacuum gauge reading becomes sufficiently low (approximately 13 Pa as a guideline).

(9) Close valve C, remove the liquid nitrogen, and leave the system undisturbed for at least 2 h. Longer standing times allow further reaction progress.

(10) Confirm that valves H, L, and S are closed, then remove traps L, K, I, and G. Wash and dry the traps.

(11) Reinstall the traps in the vacuum line, open all valves except X, Y, C, J, A, and P, and evacuate the line.

(12) Open valve P and evacuate in the same manner.

(13) After confirming with the Pirani vacuum gauge that the vacuum level is ≤0.667 Pa, close all valves except O and M.

(m) Bake-out of benzene

(1) Open valve M if it is not already open.

(2) Open valves Q, R, and the valve of trap D, and evacuate the system from the upper line.

(3) Open valve B and confirm with the Pirani vacuum gauge that a sufficient vacuum has been achieved.

(4) Close valve R.

(5) Cool trap D with liquid nitrogen.

(6) Close valve B, then open valves D and C.

(7) Wrap catalyst column C with a mantle heater and heat it to 100°C–200°C.

(8) Confirm that benzene begins to deposit in trap D, and continue heating for approximately

[*93] For acetylene trimerization, the acetylene pressure should initially be maintained slightly higher. The reaction proceeds rapidly during the first approximately 30 min and then more gradually. Heating trap E with warm air may cause rapid acetylene vaporization and a sudden pressure increase, potentially leading to rupture; therefore, cool air is normally used. If warm air is used, operate with extreme caution while monitoring the digital manometer. Because the polymerization reaction is exothermic, cooling the catalyst column with ice is also effective for accelerating the reaction and improving yield. Approximately 2 g of catalyst per 1 g of benzene is required. Under these conditions, the chemical yield is ≥85%, and isotope effects during trimerization can be neglected.

2–3 h.

(9) Heat the upper part of catalyst column C with a dryer, then close valve C.

(10) Close the valve of trap D and remove the liquid nitrogen.

(11) Leave trap D undisturbed and allow the frozen benzene to melt naturally.

(12) Remove trap D from the vacuum line and measure its weight.

(13) Subtract the tare weight of trap D to determine the mass of recovered benzene, then transfer the benzene to a glass vial for storage. Calculate the recovery rate based on the benzene mass (typically ≥80%).

(14) Store the synthesized benzene in the frozen state.

(n) Baking of low-pressure reaction vessel

(1) To eliminate cross-contamination within the reaction vessel, bake the cleaned low-pressure reaction vessel using a gas burner for 1–2 h with the lid removed and cooling water circulating.

(2) After the vessel has cooled to room temperature, it is recommended to connect it to the synthesis system and evacuate it through the upper line.

(o) Stopping the vacuum pump

(1) Confirm that all valves except valve 0 are closed, then stop the vacuum pump.

(2) Confirm that valve M is closed, then slowly open the leak valve. Do not introduce atmospheric air into the vacuum line, as this would allow moisture to enter the system.

(3) Remove liquid-nitrogen trap N, then wash and dry it.

(4) After trap N has dried, reinstall it on the synthesis system and close valve O. This prevents pump oil from entering the vacuum line.

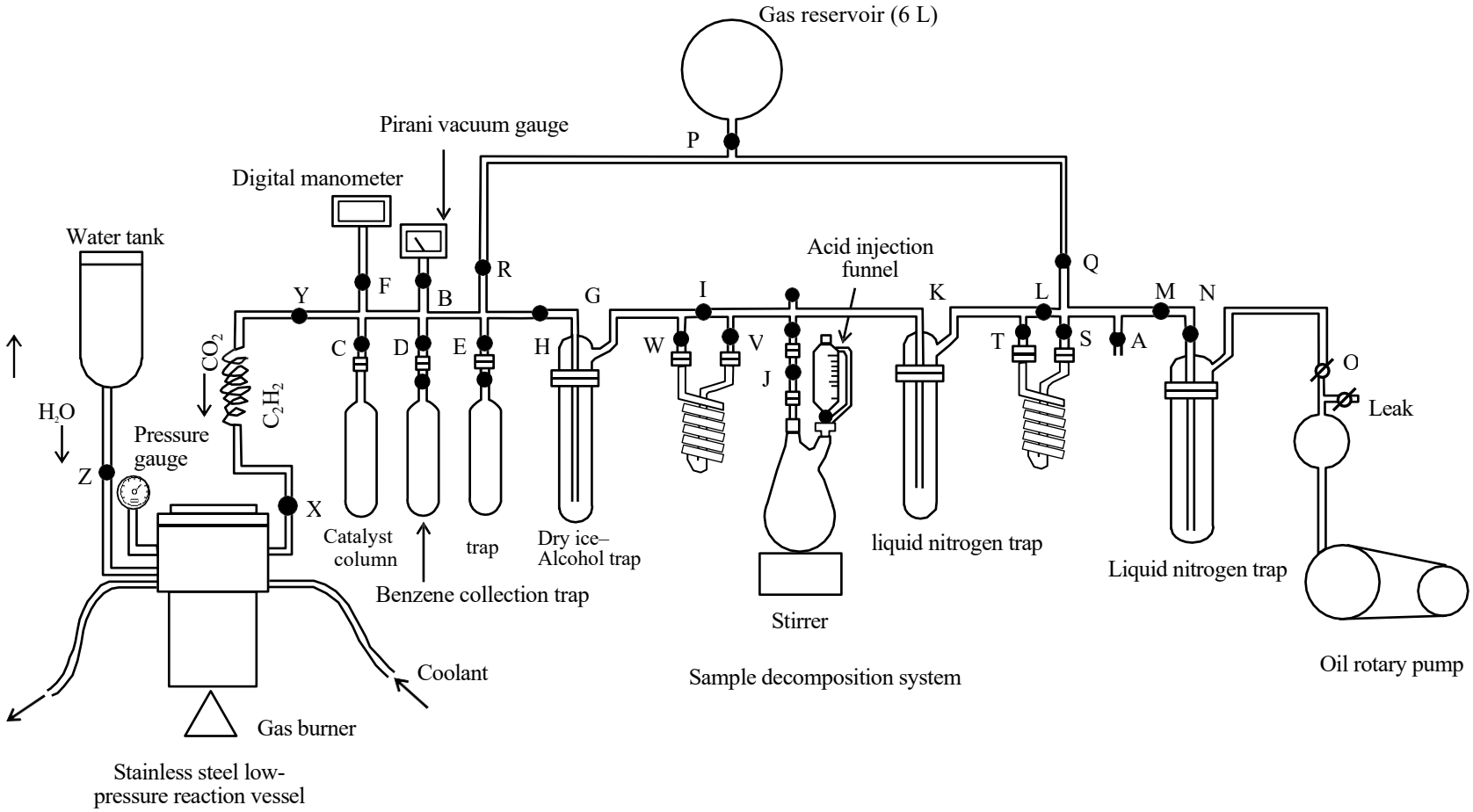


Figure 5-6 Benzene synthesis system (custom-built example)

44

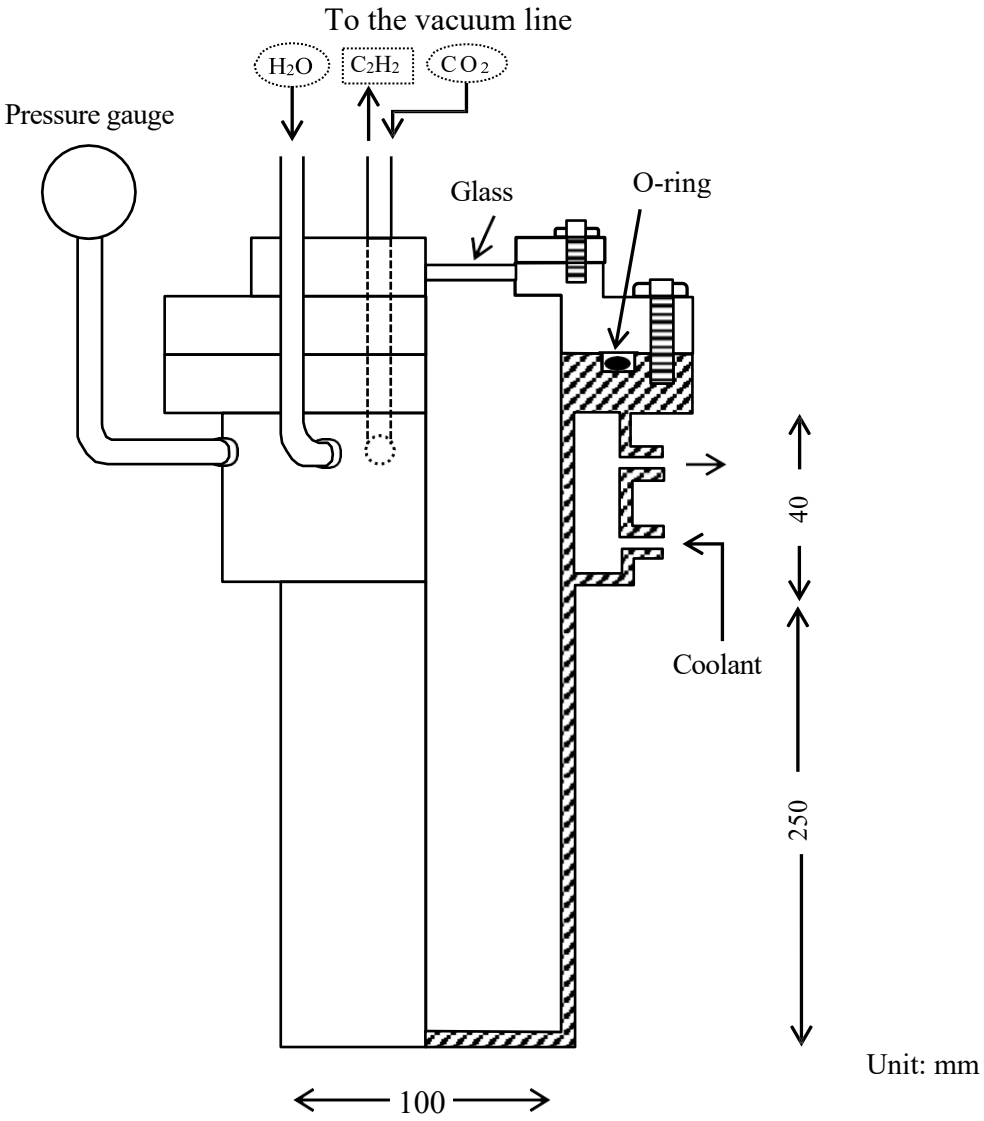


Figure 5-7 Stainless steel low-pressure reaction vessel

5.3.2 Procedure when using a commercially available benzene synthesis system

Benzene synthesis may be carried out using a commercially available benzene synthesis system, following the flow shown in Figure 5-5. This operating procedure describes the valve operations for the benzene synthesis system shown in Figure 5-8 and is applicable only to systems of similar configuration.

In this procedure, CO_2 is generated from calcium carbonate as described below and subsequently converted to benzene for measurement.

5.3.2.1 Equipment, instruments, and reagents

(1) Equipment

1) Commercial benzene synthesis system (Figure 5-8)

(2) Instruments

Not used.

(3) Reagents

1) Metallic lithium[*94]: Wheel-shaped or rod-shaped, with purity of ≥99.8%[*95]. Metallic lithium immersed in oil shall not be used, as it may cause carbon contamination.
2) Phosphorus pentoxide
3) Ascarite[*96, *97]
4) Dry ice–alcohol coolant
5) Liquid nitrogen
6) Catalyst: Trivalent chromium–alumina pellets

[*]94 Classified as a Class III hazardous material (spontaneously combustible and water-reactive substances) under the Fire Service Act. Avoid contact with air, water, moisture, flames, sparks, or other high-temperature objects. Store under a protective liquid or in an inert gas atmosphere such as argon, and subdivide for storage as necessary.

[*]95 Metallic lithium is normally stored in a vacuum desiccator; however, long-term storage is difficult. Commercially available lithium sealed in aluminum bags under argon gas is recommended, and it is preferable to use one package per analytical batch.

[*]96 Substances that require labeling under the Industrial Safety and Health Act (i.e., substances that may endanger workers or cause health impairment) must be clearly labeled, accompanied by Safety Data Sheets, and subjected to risk assessments, including the implementation of risk-reduction measures. Employers are required to inform and educate workers regarding proper handling of these substances.

[*]97 Substances subject to the Poisonous and Deleterious Substances Control Act (i.e., substances posing a high risk of acute toxicity-related health hazards) must be stored and displayed in areas labeled as “Non-Pharmaceutical Poisonous Substances” or “Non-Pharmaceutical Deleterious Substances.” Appropriate measures must be taken to prevent theft, loss, leakage, and related incidents.

5.3.2.2 Procedure

(a) Decomposition of the sample

(1) Place 40 g of calcium carbonate into the acid decomposition flask shown in Figure 5-9, then add 300 mL of pure water and a stirring bar.

(2) Add 200 mL of phosphoric acid (1+1) to a separatory funnel, assemble the acid decomposition flask, and connect it to Joint-1 of the benzene synthesis system shown in Figure 5-8.

(3) Cool trap (T-1) with a dry ice–alcohol coolant, and cool traps (T-2) and (T-3) with liquid nitrogen.

(4) To evacuate air from the acid decomposition flask, open valve (V-17), set valve (V-14) to the red direction, and open valve (V-1). Evacuate until gauge (G-1) reaches −25 inHg, then close valve (V-1).

(5) After approximately 1–2 min, close valve (V-17).

(6) Turn on the stirrer to thoroughly mix the calcium carbonate and water, then open valve (V-1).

(7) Adjust the separatory funnel valve to allow phosphoric acid to drip slowly into the flask, decomposing the calcium carbonate and generating CO_2. When gauge (G-1) reaches approximately −15 inHg, open valves (V-2), (V-3), (V-4), (V-5), (V-6), and (V-8) to collect the generated CO_2.

(8) When the pressure indicated by gauge (G-1) decreases to −20 inHg, close valve (V-2). When the pressure subsequently rises to −10 to −5 inHg, reopen valve (V-2) to collect CO_2.

When gauges (G-1) and (G-2) indicate the same pressure, close valve (V-2) and wait for the pressure at gauge (G-1) to rise again. Repeat this operation until decomposition is complete and no further CO_2 is generated.

(9) When the calcium carbonate has completely decomposed and the solution becomes transparent, open valves (V-2) and (V-9) to collect CO_2 dissolved in the solution.

(10) After closing valves (V-1), (V-2), and (V-9), disconnect the acid decomposition flask from the benzene synthesis system.

(11) Replenish liquid nitrogen in traps (T-2) and (T-3), then remove the liquid nitrogen while monitoring the pressure indicated by gauge (G-1). Open valve (V-9) and evacuate the system.

(12) Close valves (V-5) and (V-9), then open valves (V-11), (V-12), and (V-13) in that order to transfer CO_2 to the storage tank.

(13) After all CO_2 in the traps has vaporized, close valves (V-12) and (V-13). Cool the microtrap with liquid nitrogen and collect all CO_2 from traps (T-1) and (T-2).

(14) After closing valve (V-11), open valves (V-12) and (V-13), remove the liquid nitrogen from the microtrap, and transfer the CO_2 into the storage tank.

(b) Benzene synthesis

(1) Evacuate air from all traps and the reaction chamber and allow them to dry completely.

(2) Close the evacuation valves and confirm, using the gauges, that no leaks are present in

the system.

(3) Open the leak valve of the reaction chamber and remove the chamber.

Quickly place metallic lithium into the chamber (approximately 18 g per 10 L of CO_2). Reinstall the chamber, then open valves (V-15) and (V-17) to evacuate the chamber while securely fixing it to the system.

(4) Circulate cooling water to cool the reaction chamber.

(5) Install the electric furnace and, while evacuating, raise the reaction chamber temperature to 800°C so that the metallic lithium spreads uniformly over the bottom. Metallic lithium begins to melt at approximately 450°C.

(6) Lower the reaction chamber temperature to 620°C.

(7) Close valves (V-15) and (V-17), and set valve (V-14) to the blue line direction.

(8) Slowly open valve (V-15) and introduce CO_2 into the reaction chamber, allowing it to react with molten lithium to form lithium carbide.

(9) When all CO_2 has reacted and gauges (G-3), (G-4), and (G-6) reach −30 inHg, switch valve (V-14) to the red direction and open valve (V-17) to evacuate the system. Raise the reaction chamber temperature to 800°C and maintain this condition for 1 h.

(10) Remove the electric furnace, close valves (V-15) and (V-17), and allow the reaction chamber to cool to room temperature.

(11) Pack the acetylene purification column with phosphorus pentoxide (drying agent) and Ascarite (CO_2 absorbent) in equal proportions, and install the column.

(12) After closing valves (V-4) and (V-5), open valve (V-19) slightly to reduce pressure in the purification column. Then open valves (V-5) and (V-9) to evacuate the line.

(13) Confirm the valve configuration for acetylene collection:

Valves closed: (V-1), (V-2), (V-4), (V-7), (V-9), (V-10), (V-11), (V-12), (V-17), and (V-22)

Valves open: (V-3), (V-5), (V-6), (V-8), (V-13), (V-18), and (V-19)

(14) After the reaction chamber has cooled sufficiently, cool trap (T-1) with a dry ice–alcohol coolant and traps (T-2) and (T-3) with liquid nitrogen.

(15) Open valve (V-15) and set valve (V-14) to the red line direction.

(16) While monitoring gauges (G-1) or (G-6), slowly open valve (V-16) and drip purified water onto the lithium carbide to generate acetylene.

(17) When gauge (G-1) reaches −15 inHg, open valve (V-2). When gauges (G-1) and (G-2) indicate similar pressures, close valve (V-2) to collect acetylene.

(18) While the pressure at gauge (G-1) increases toward −15 inHg, open valve (V-9) to evacuate hydrogen generated simultaneously with acetylene.

(19) Repeat steps (17) and (18). After the lithium carbide has fully reacted, close valve (V-16), then open valves (V-2) and (V-9) and evacuate the reaction chamber to collect acetylene dissolved in the solution.

(20) After closing valve (V-5), carefully monitor gauge (G-5) while removing liquid nitrogen from the traps. Then open valve (V-9) and evacuate the system.

(21) After closing valve (V-9), open valves (V-11) and (V-13) to transfer acetylene from the traps to the storage tank.

(22) After all acetylene in the traps has vaporized, close valve (V-13). Cool the microtrap with liquid nitrogen and collect residual acetylene from the traps and lines.

(23) After closing valve (V-11), open valve (V-13) and remove the liquid nitrogen from the microtrap.

(24) After closing valves (V-6) and (V-8), open valves (V-11) and (V-7) to introduce acetylene from the storage tank into the catalyst column and synthesize benzene by polymerization. Use approximately 70 mL of catalyst, dried at 400°C for at least 3 h under evacuation.

(25) Once polymerization begins, cool the column with water.

(26) When gauge (G-4) reaches −20 inHg, stop cooling and allow the system to stand overnight to complete polymerization.

(27) After overnight standing, open valve (V-9) and evacuate trap (T-3).

(28) After closing valves (V-9) and (V-11), cool trap (T-3) with a dry ice–alcohol coolant.

(29) Open valves (V-7) and (V-8), then gradually open valve (V-9) while monitoring gauge (G-5). Heat the catalyst column to 100°C over 2–3 h to release and collect benzene retained in the catalyst.

(30) Close valves (V-7), (V-8), and (V-9), and remove the catalyst column.

(31) Remove the dry ice–alcohol coolant from trap (T-3) and allow it to warm to room temperature, melting the frozen benzene.

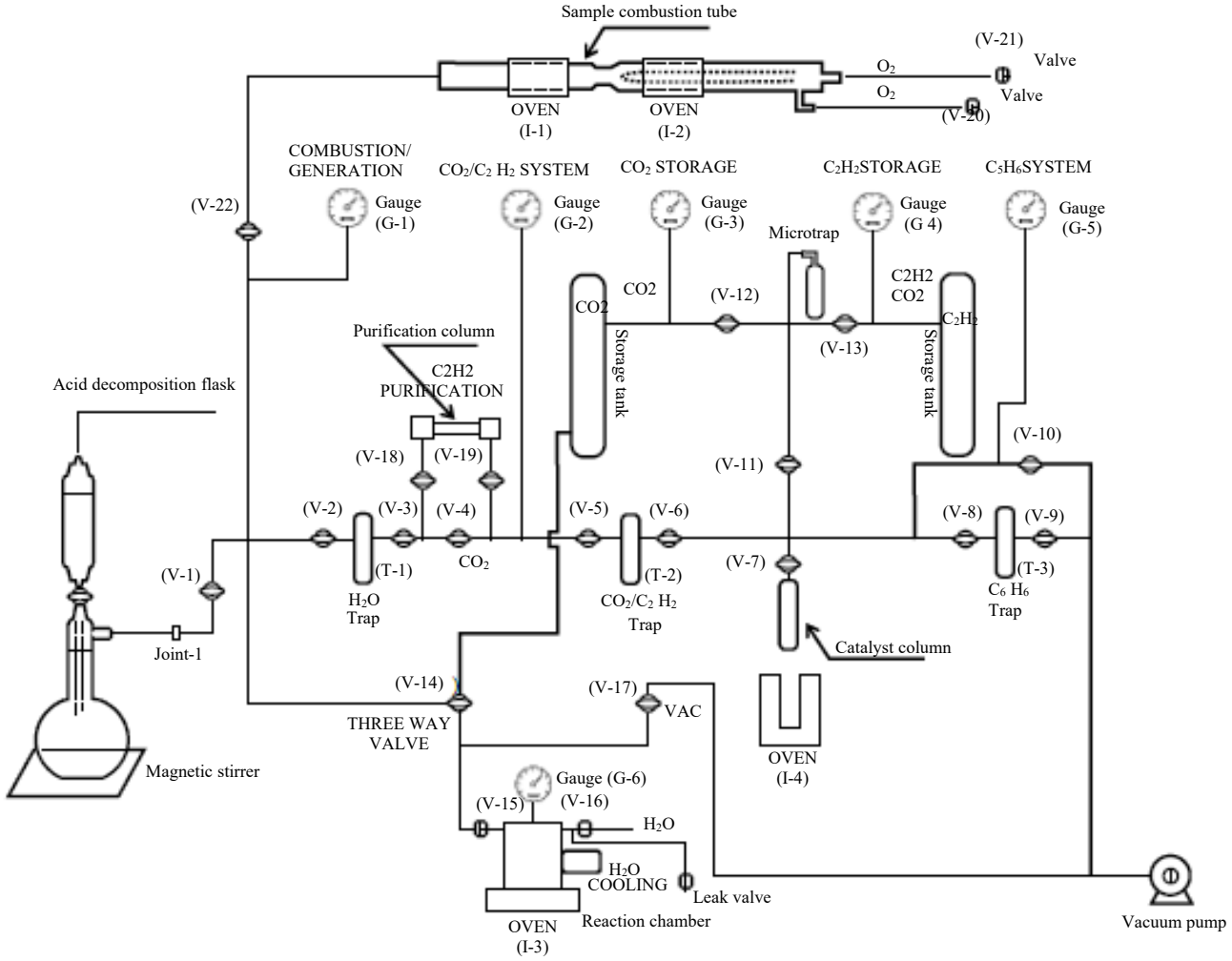


Figure 5-8 Commercially available benzene synthesis system (system diagram)

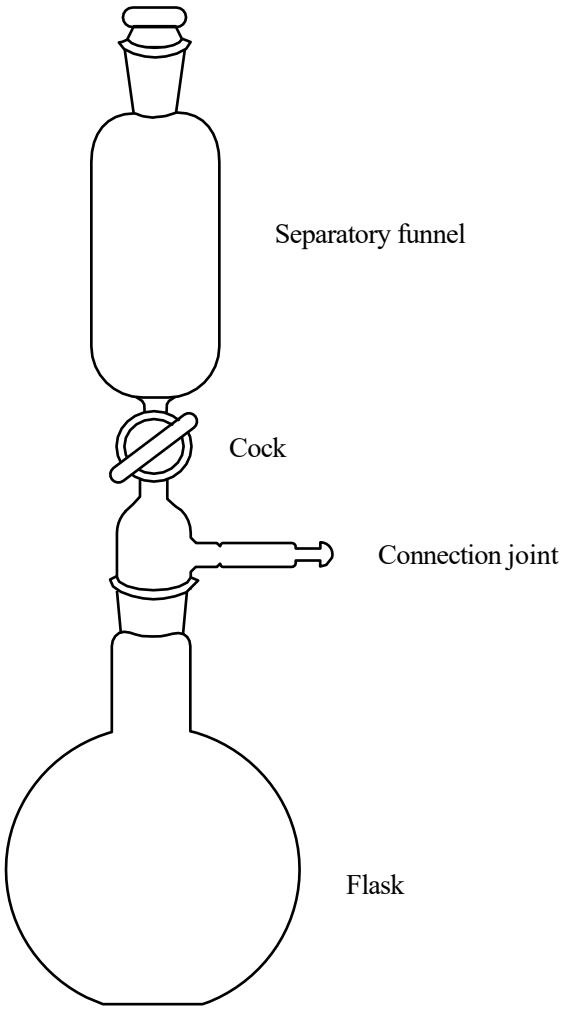


Figure 5-9 Acid decomposition flask

5.3.3 Measurement

The settings of the lower-level discriminator (LLD) and upper-level discriminator (ULD) for the ^{14}C measurement channel shall be determined in advance by evaluating the figure of merit (FOM; performance index) using a strong standard source and a blank sample. The energy region that yields the highest FOM is then selected. For measurements of weak radioactivity, including environmental samples, measurement conditions shall be chosen to minimize counting error, using the FOM as a guiding metric. The FOM is defined as $FOM = \varepsilon^2/r_0$, where ε is the counting efficiency and r_0 is the background counting rate (cpm). Measurement conditions that maximize this value shall be adopted. To determine the counting efficiency, measurements are performed repeatedly for 50 min per run using a set of three samples: a NIST oxalic acid standard, the sample, and a blank measurement sample prepared from marble. Measurements shall be repeated at least 10 times, resulting in a total counting time of ≥ 500 min. When the number of counts is small, longer measurement times shall be used to improve measurement accuracy.

Because the quenching of the benzene sample changes little over time, the counting efficiency determined using this procedure may continue to be applied, provided that no notable changes occur in the measurement conditions.

5.3.3.1 Equipment, instruments, and reagents

(1) Equipment

1) Low-background liquid scintillation counter

(2) Instruments

1) Balance: Minimum readability of 0.0001 g
2) Mini vials: Commercially available low-potassium glass vials with a capacity of 7 mL[*98].
3) Vial holder: Commercially available wide-mouth low-potassium glass vials with a capacity of 20 mL

[*98] The capacity of the measurement vials may be adjusted as appropriate depending on the sample amount. Fluoroplastic containers may be used; however, polyethylene containers should be avoided because of their susceptibility to benzene and toluene contained in scintillators.

(3) Reagents

1) Toluene[*99,*100,*101] : Special grade

・ Liquid scintillator solution: A toluene solution containing 5 w/v% butyl-PBD. Dissolve 5 g of the fluorescent agent 2-(4-biphenyl)-5-tert-butylphenyl-1,3,4-oxadiazole (butyl-PBD) in 100 mL of toluene. Store the solution in a brown bottle (or a light-shielded bottle wrapped in aluminum foil) in a cool, dark place.

*99 Hazardous substances that require labeling under the Industrial Safety and Health Act (i.e., substances that may endanger workers or cause health impairment) shall be clearly labeled, accompanied by Safety Data Sheets, and subjected to risk assessments, including the implementation of risk-reduction measures. Employers are required to inform and educate workers regarding the proper handling of these substances.

*100 Substances subject to the Poisonous and Deleterious Substances Control Act (i.e., substances posing a high risk of acute toxicity-related health hazards): Storage and display areas shall be labeled as "Non-Pharmaceutical Poisonous Substances" or "Non-Pharmaceutical Deleterious Substances," and appropriate measures shall be implemented to prevent theft, loss, leakage, or similar incidents.

*101 Classified as a Class IV hazardous material (flammable liquid) under the Fire Service Act. The following precautions are required: open flames shall be strictly avoided; the material shall be stored and handled below its flash point; it shall be kept separate from Category I and Category V hazardous substances; measures shall be implemented to prevent static electricity; and when transferring to smaller containers, they shall not be filled to full capacity to prevent rupture due to thermal expansion.

5.3.3.2 Setting of measurement conditions

(a) Setting of the measurement window

Most commercially available liquid scintillation counters are equipped with a multichannel pulse-height analyzer, allowing the energy spectrum to be displayed during measurement. The procedure for setting the measurement window for the ^{14}C measurement channel using such an instrument is described below.

(1) Approximately 1 h before starting counting, place the two samples—the standard sample prepared in Section 5.2 and the blank measurement sample prepared in Section 5.1—into the sample changer. Insert the standard sample into the detector.
(2) Measure for at least 1000 min using the ^{14}C measurement channel and observe the ^{14}C spectrum. Set the LLD at approximately the equivalent of 10 keV, and successively shift the ULD to 20, 30, …, 100 keV. Determine the counting rate (cpm) within each corresponding window.
(3) Insert the blank measurement sample into the detector and measure under the same conditions for at least 1000 min. Set the LLD and vary the ULD in the same manner, and determine the counting rate (cpm) for each window.
(4) For each ULD setting, calculate the counting efficiency ε using the method described in Section 5.3.4.
(5) Plot a graph with the ULD setting on the horizontal axis and the FOM on the vertical axis.
(6) Reset the ULD to the value that provides the maximum FOM.

(b) Measurement of channel ratio based on a quenching indicator

The external standard channel ratio, which represents the degree of quenching in the measured sample, is measured automatically by setting the LLD to approximately 80–90 channels without applying a specific measurement window. The measurement procedure is described below.

First, an external γ-ray source (^{137}Cs) is placed near the measurement sample, and the combined $\gamma + \beta$ spectrum (Compton electron spectrum from γ rays plus the ^{14}C β-ray spectrum) is measured. The γ-ray source is then removed, and the β-ray spectrum alone is measured.

For each channel, the accumulated β-only counts are subtracted from the accumulated $\gamma + \beta$ counts to obtain a pure Compton spectrum attributable solely to γ rays. From this spectrum, the channel that divides the total area (total counts) from the LLD to the high-energy region by a specified ratio is determined. This channel number is multiplied by a channel-specific coefficient to obtain a quenching indicator value for the sample.

Using this method, the NIST oxalic acid standard, the unknown sample, and the marble blank sample are prepared and measured as a set within a short time interval, resulting in generally comparable quenching levels. The quenching indicator is used to confirm this condition, and

no correction of counting efficiency based on the quenching indicator value is applied.

5.3.3.3 Preparation and measurement of samples

The synthesized benzene is prepared as a measurement sample according to the procedure below and measured using a liquid scintillation counter.

(1) Prepare two mini vials for measurement (capacity: 7 mL), one for the sample and one for the background sample.
(2) Accurately weigh the empty vials.
(3) Using a micropipette, accurately aliquot A mL of the synthesized benzene sample and transfer it into the vial, then cap the vial.
(4) Accurately weigh the vial containing the benzene.
(5) Add 2 mL of liquid scintillator solution to the vial using a micropipette, followed by B mL of ^{14}C-free benzene*102. Adjust the volumes so that A + B = 4 mL. Securely cap the vial*103 and mix thoroughly*104.
(6) Wipe the vial thoroughly with paper moistened with alcohol, place it in a vial holder, and leave it inside the measuring instrument overnight.
(7) Place the blank measurement sample and the standard sample in the sample changer.
(8) Set the measurement window for the ^{14}C measurement channel.
(9) Alternately measure the quenching indicator and perform the ^{14}C measurement (measurement time: 50 min) for each sample in sequence. Repeat the procedure at least 10 times to obtain a total counting time of at least 500 min.
(10) After completing the measurements, use the obtained data to determine the specific radioactivity of ^{14}C of the sample according to the calculation method described in Section 5.3.4 or Explanation C.4.1.1.



Liquid scintillator solution:	2 ml
+	
Benzene:	4 ml
(sample benzene + ^{14}C-free benzene)	
Total volume	6 ml

Note: The actual measurement sample is not separated into two layers.

[Low-potassium glass]

Figure 5-10 Example of the composition of a measurement sample in the benzene synthesis method

*102 Benzene synthesized from marble or similar materials may be used. Reagent-grade benzene may also be used.
*103 A Teflon inner liner approximately 0.5 mm thick inside the cap can prevent evaporative loss of benzene.
*104 See Figure 5-10.

5.3.4 Calculation of specific radioactivity of ^{14}C

The specific radioactivity of ^{14}C of a sample is calculated using the following equations. For a worked numerical example, refer to Explanation C.

$$A = \left(\frac{N_s}{t_s} - \frac{N_b}{t_b}\right) \times \frac{1}{\varepsilon} \times \frac{1}{W_S}$$

$$\sigma = \sqrt{\frac{N_s}{{t_s}^2} + \frac{N_b}{{t_b}^2}} \times \frac{1}{\varepsilon} \times \frac{1}{W_S}$$

A: Specific radioactivity of ^{14}C of the sample (Bq/gC)

σ: Uncertainty due to counting statistics

N_s: Number of counts of the measurement sample

t_s: Sample measurement time (s)

N_b: Number of counts of the background measurement sample

t_b: Measurement time for the background (s)

W_s: Amount of carbon in the measured sample (gC)

ε: Counting efficiency for ^{14}C

The amount of carbon in the measured sample, W_s, is calculated from the mass of benzene used for measurement as follows:

$$W_S = W_c \times \frac{72}{78}$$

W_c: Mass of benzene used in the measurement (g)

The counting efficiency ε is calculated using a standard material as follows:

$$\varepsilon = \left(\frac{N_{source}}{t_{source}} - \frac{N_b}{t_b}\right) \times \frac{1}{W_{source}} \times \frac{1}{0.3042}$$

N_{source}: Number of counts of the NIST oxalic acid standard

t_{source}: Counting time for the NIST oxalic acid standard (s)

W_{source}: Amount of carbon in the NIST oxalic acid sample (gC)

0.3042: Specific radioactivity of ^{14}C of NIST oxalic acid (SRM 4990C) as of 2023[*105,*106] (Bq/gC)

If radioactivity per unit mass or per unit volume (rather than specific radioactivity of ^{14}C) is required, the carbon content of the sample shall be determined in advance using an elemental

[*105] "As of 2023" is shown as an example. The value shall be corrected to the time of measurement. Refer to Explanation A for the calculation method.

[*106] When a standard material other than SRM 4990C is used, the specific radioactivity of ^{14}C of that standard material shall be applied.

analysis method or other appropriate methods[*107].

The radioactivity concentration is then calculated as follows:

$$A_N = A \times \frac{R_c}{100}$$

A_N : Radioactivity concentration of the sample (Bq/kg, Bq/L, etc.)

N : Specific radioactivity of ^{14}C of the sample (Bq/gC)

R_c : Carbon content of the sample (%)

5.4 Liquid scintillation measurement method using carbon dioxide absorption

In this method, the specific radioactivity of ^{14}C is determined by absorbing CO_2 in air into a scintillator solution containing a CO_2 absorbent, followed by measurement using a liquid scintillation counter.

5.4.1 Preparation of measurement samples

Calcium carbonate prepared using the methods described in Chapters 2, 3, 4, and 5 is decomposed by reaction with an acid[*108]. The CO_2 generated during this reaction is absorbed into an absorption solution to prepare the measurement sample.

5.4.1.1 Equipment and instruments

(1) Equipment

Not used.

(2) Instruments

1) Sampling bags: Aluminum bags
2) Three-neck round-bottom flask: 500 mL capacity
3) Cooling condenser (coil type)
4) Separatory funnel: 300 mL
5) Fluoroplastic measurement bottles: 100 mL capacity[*109]
6) Gas washing bottles: 25 and 250 mL
7) Three-way cock: Teflon
8) Screw-type clamp
9) Air pump: Diaphragm type with adjustable flow rate of 0–50 mL/min
10) Stirrer

[*107] Other methods include calculations based on the recovered amount of CO_2 or on the stoichiometric carbon content of calcium carbonate.

[*108] There is also a method in which purified CO_2 obtained from the sample is absorbed directly into a CO_2 absorbent; however, this method is not covered here. For details, refer to JAEA Technology 2009-51, JAEA Technology 2016-013, etc.

[*109] The capacity of the measurement vials may be adjusted as appropriate depending on the sample amount.

(3) Reagents

1) Hydrochloric acid[*110, *111, *112]: Special grade

・ Hydrochloric acid (1+1): Mix equal parts of hydrochloric acid and pure water.

2) Calcium hydroxide: Special grade; dissolved in pure water with heating to prepare a saturated solution.

・ Saturated calcium hydroxide solution: Dissolve calcium hydroxide in pure water with heating and use the supernatant liquid after undissolved solids have settled.

3) CO_2 absorbent[*113]: For liquid scintillation counting, use a colorless, transparent[*114] liquid that mixes well with the scintillator to form a homogeneous solution, or a solid that readily dissolves in the scintillator to produce a colorless, transparent solution.

4) Methanol[*111,*112,*115]: Special grade

5) Toluene-based scintillator: Dissolve 4 g of 2,5-diphenyloxazole and 0.3 g of 1,4-bis[2-(5-phenyloxazolyl)]benzene in 1 L of toluene. Store in a brown bottle[*116] in a cool, dark place.

6) Silica gel: Dehydrate on a hot plate immediately before use.

7) Nitrogen gas: Purity of 99.999%.

5.4.1.2 Procedure

(a) Preparation of the system

1) Assemble the CO_2 absorption system as shown in Figure 5-11.

2) Place a stir bar at the bottom of the three-neck round-bottom flask.

3) Accurately weigh 8.33 g of calcium carbonate (equivalent to 1 g of carbon)[*117] and place it into the flask.

4) Pour 120 mL of hydrochloric acid (1+1) into the separatory funnel.

5) Remove the stopper from the top of the separatory funnel, insert the nitrogen gas hose, and flush the funnel with nitrogen at approximately 300 mL/min for approximately 1 min to replace the internal air.

6) Replace the internal atmosphere of sampling bag 1 with nitrogen gas three times, then introduce approximately 3 L of nitrogen gas. Close the sampling bag 1 side of three-way cock

---

*110 Class III substances under the Ordinance on Prevention of Hazards due to Specified Chemical Substances (substances that may cause acute poisoning due to large-volume leakage): Measures must be implemented to reduce exposure concentrations, such as the installation of local exhaust ventilation systems.

*111 Hazardous substances that require labelling under the Industrial Safety and Health Act (i.e., substances that may endanger workers or cause health impairment) must be clearly labelled, accompanied by Safety Data Sheets, and subjected to risk

*112 Substances subject to the Poisonous and Deleterious Substances Control Act (i.e., substances posing a high risk of acute toxicity-related health hazards): Storage and display areas must be labelled as “Non-Pharmaceutical Poisonous Substances” or “Non-Pharmaceutical Deleterious Substances,” and appropriate measures must be taken to prevent theft, loss, leakage, and similar incidents.

*113 Commercially available CO_2 absorbents include Carbo-Sorb E (PerkinElmer).

*114 Coloration reduces counting efficiency during liquid scintillation measurement.

*115 Classified as a Class IV hazardous material (flammable liquid) under the Fire Service Act. Open flames must be avoided. Store and handle below the flash point, keep segregated from Category I and Category V hazardous substances, implement measures to prevent static electricity, and avoid filling containers to full capacity during transfer to prevent rupture due to thermal expansion.

*116 A transparent bottle shielded from light (e.g., wrapped with aluminum foil) may also be used.

*117 If the calcium carbonate content of the sample is less than 8.33 g, add marble blank to obtain a total mass of 8.33 g.

(1).

7) After closing the gas washing bottle side of three-way cock (3), replace the atmosphere of the system—from the three-neck flask to sampling bag 2—with approximately 3 L of nitrogen gas, and exhaust the nitrogen gas (containing residual air) from sampling bag 2 using the air pump. Repeat this operation three times to fully replace the system atmosphere with nitrogen.
8) Add the CO_2 absorbent to the first and second gas washing bottles used for CO_2 collection.
9) Add 200 mL of saturated calcium hydroxide solution to the 250 mL gas washing bottle. This solution is used to check for CO_2 leakage during the absorption process.
10) Close the nitrogen-cylinder side of three-way cock (1), the separatory funnel side of three-way cock (2), and the sampling bag 2 side of three-way cock (3).
11) Open the stopcock of the first gas washing bottle and operate the air pump at a flow rate of 50 mL/min for approximately 2 min to draw nitrogen gas from sampling bag 2, thereby replacing the atmosphere in the first and second gas washing bottles with nitrogen.
12) Stop the air pump and close the gas washing bottle side of three-way cock (3).

(b) Decomposition of the sample (calcium carbonate)

1) Close the sampling bag 1 side of three-way cock (2) and start the flow of cooling water.
2) Open the cock of the separatory funnel and slowly add 120 mL of hydrochloric acid (1+1) dropwise to decompose the calcium carbonate. After adding approximately 20 mL, stir with a stirrer to promote the reaction.
3) Confirm that the generated CO_2 is being collected in sampling bag 2[*118]. When the reaction is complete, close the condenser-side port of three-way cock (3).

(c) Absorption of CO_2

1) Slowly draw the gas using the air pump (flow rate: 50 mL/min) and pass the CO_2 collected in sampling bag 2 through the CO_2 absorbent.
2) When most of the CO_2 in sampling bag 2 has been discharged, temporarily stop the air pump.
3) Close the sampling bag 2 side of three-way cock (3), fully open all three ports of three-way cock (2), and confirm that three-way cock (1) is closed on the nitrogen cylinder side.
4) Slowly draw the gas using the air pump (flow rate: 50 mL/min) and pass the CO_2 remaining in the system, together with the nitrogen gas in sampling bag 1, through the CO_2 absorbent[*119].
5) When most of the nitrogen gas in sampling bag 1 has been discharged, temporarily stop the air pump.
6) Close the sampling bag 1 side of three-way cock (1) and close the gas washing bottle side of three-way cock (3).

---

[*]118 When calcium carbonate reacts with hydrochloric acid, CO_2 is produced vigorously. Therefore, the CO_2 is first collected in sampling bag 2 and then passed through a CO_2-absorbing solution at a constant flow rate.

[*]119 Depending on the CO_2 absorbent used, precipitates formed during absorption may clog the tip of the absorption tube. In such cases, stop the air pump, close the cock of the first gas washing bottle, seal the silicone tube upstream of the cock using a screw-type clamp, remove it, and dissolve the precipitate by adding 0.5 mL of methanol into the absorption tube.

7) Using approximately 2 L of nitrogen gas from the cylinder, collect any CO_2 remaining in the system into sampling bag 2.
8) Close the condenser-side port of three-way cock (3). Then, using the air pump (flow rate: 50 mL/min), slowly draw the gas and pass the nitrogen from sampling bag 2 (which contains a small amount of CO_2) through the CO_2 absorbent.
9) Discharge all nitrogen gas from sampling bag 2 and stop the air pump.
10) Wash the absorption tube in the first gas washing bottle with 5 mL of methanol (subtract the amount used if methanol was added to dissolve precipitates formed inside the absorption tube during absorption)[*120], and add the washing liquid to the absorption solution.
11) Combine the absorption solution from the second gas washing bottle with that from the first. Rinse the second gas washing bottle with 5 mL of the toluene-based scintillator, add the rinse to the combined absorption solution, and seal the container.
12) Gently shake to dissolve any precipitates and use the solution as the measurement sample.

5.4.2 Measurement

5.4.2.1 Equipment, instruments, and reagents

(1) Equipment

1) Low-background liquid scintillation counter

(2) Instruments

Not used.

(3) Reagents

Not used.

5.4.2.2 Setting of measurement conditions

Refer to Section 5.3.3.2 Setting of measurement conditions.

5.4.2.3 Sample measurement

Refer to Section 5.3.3.3, Preparation and measurement of samples.

(1) Prepare vials for measurement. Fluoropolymer vials (100 mL) are preferred; however, low-potassium glass or fluoropolymer vials (20 mL) may also be used.
(2) Accurately weigh the tare of the vials.
(3) Transfer the measurement sample prepared in Section 5.4.1 into a vial.
(4) Accurately weigh the vial containing the measurement sample.

[*]120 If methanol was used to dissolve precipitates formed inside the absorption tube during absorption, subtract that amount from the 5 mL used for washing.

(5) Thoroughly wipe the vial with paper moistened with alcohol, place it in a vial holder, and set it on the sample changer.
(6) Set the blank measurement sample and the standard sample on the sample changer.
(7) Set the measurement window for the ^{14}C measurement channel.
(8) Alternately measure the quenching indicator value and perform the ^{14}C measurement (measurement time: 50 min) for each sample in sequence. Repeat the procedure at least 10 times to achieve a total counting time of at least 500 min.

5.4.3 Calculation of specific radioactivity of ^{14}C

Refer to Section 5.3.4 or Explanation C.4.1.1.

When calculating the specific radioactivity of ^{14}C, the amount of carbon in the sample is obtained from the mass of calcium carbonate used. A mass of 8.33 g of calcium carbonate corresponds to 1 gC[*121].

[*121] Assuming a formula weight of 100 for calcium carbonate and an atomic weight of 12 for carbon, the amount of carbon contained in 1 g of calcium carbonate is 12/100 = 0.12 g. Thus, the amount of calcium carbonate required to obtain 1 g of carbon is 1/0.12 ≈ 8.33 g.

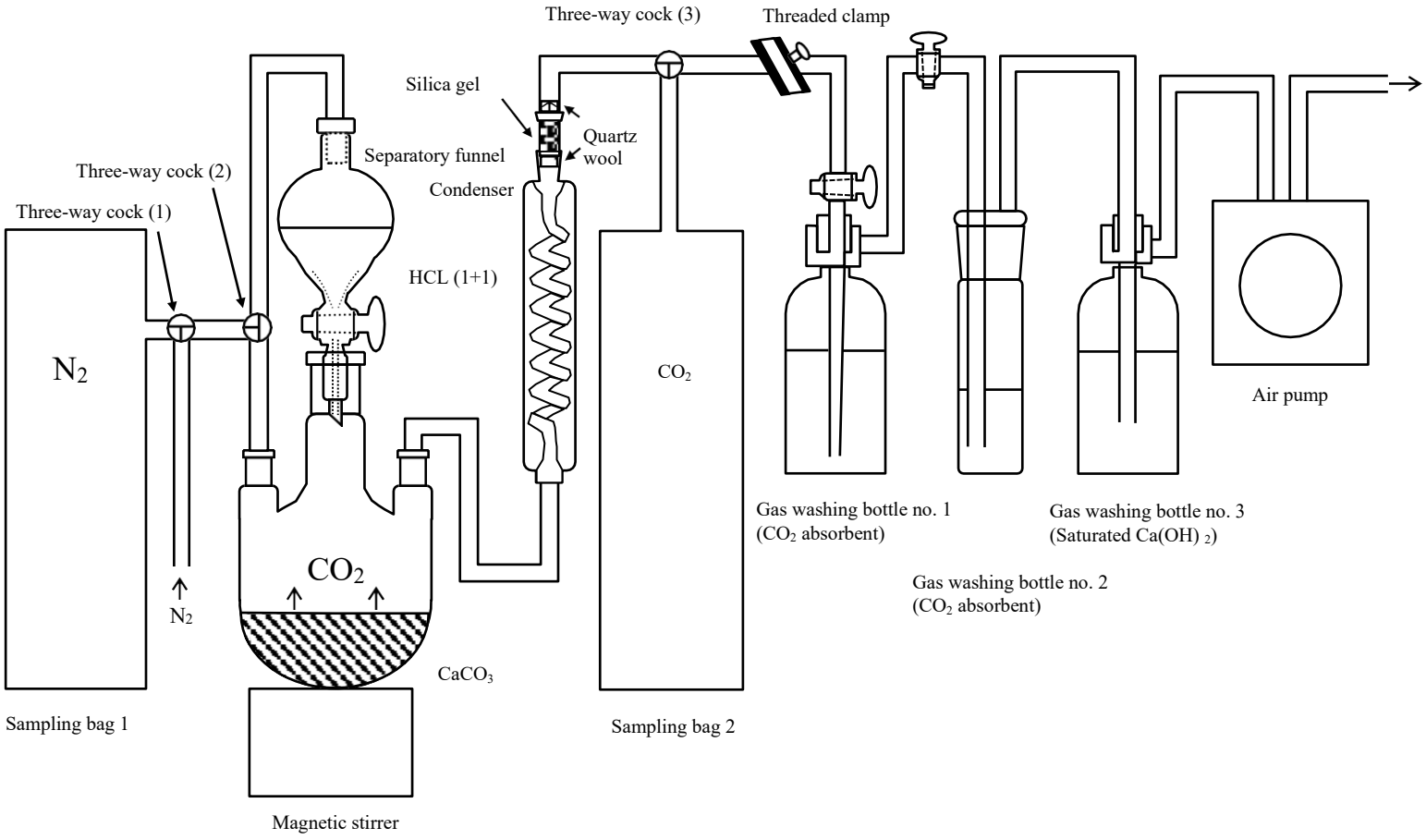


Figure 5-11 Example of a CO_2 absorption system

5.5 Uncertainty

Uncertainty of measurement is used as an indicator of the reliability of a measurement result. Uncertainty of a measurement is defined as “a parameter, associated with the result of a measurement, that characterizes the variation of values that could reasonably be attributed to the quantity being measured”[*122]. The uncertainty of a measurement does not represent the variation of individual measurement results, but rather the potential variability of a series of measurements. In conventional radiocarbon analyses, the uncertainty arising from counting statistics (counting error) in radioactivity measurements is commonly evaluated and reported. However, in radiocarbon analysis of environmental samples, sources of uncertainty exist throughout the entire analytical process, including pretreatment and calibration of measurement instruments. Therefore, evaluating the uncertainty associated with each step is crucial. By evaluating uncertainty, it becomes possible to judge agreement or disagreement among radiocarbon analysis results obtained by different analytical institutions in proficiency testing and interlaboratory comparisons. Furthermore, by identifying the steps that contribute most to uncertainty and taking actions to make the uncertainty more appropriate, it is possible to improve the quality of analytical results.

For methods of evaluating uncertainty in radiocarbon analysis, refer to Explanation B.

5.6 Lower detection limit

The lower detection limit in radioactivity measurements depends on factors such as the sample quantity, measurement duration, and background count rate. The target detection limit is established in accordance with the analytical objectives and the intended measurement purpose. Generally, a radionuclide is considered “detected” or “not detected” when the net counting rate exceeds three times the statistical uncertainty of the net counting rate. Calculation of the lower detection limit indicates the minimum level of radioactivity concentration that can be detected in the measurement. Notably, if a sample contains radioactivity greater than the lower detection limit, it will be detected in most cases. However, radioactivity below the detection limit does not necessarily result in a “not detected” outcome, and detection may still occur.

Methods for calculating the lower detection limit include Cooper’s method[*123], the Kaiser method[*124,*125] described in the first edition of this measurement method, and the evaluation method specified in the international standard ISO 11929[*126]. For each concept of the lower detection limit, considering the distribution of measurement values is necessary. When a given measurement target is measured a sufficiently large number of times, the distribution of the measurement values becomes

[*]122 JIS Z 8404-1：測定の不確かさ−第 1 部, JIS Z 8404-1:2018 (2018)

[*]123 J.A Cooper: Factors determining the ultimate detection sensitivity of Ge (Li) gamma-ray spectrometers, Nuclear Instruments and Methods, 82, 273-277 (1970)

[*]124 H.Kaiser : Zum Problem der Nachweisgrenze, Analytisehe Chemie, 209, 1-18 (1965)

[*]125 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 & Applied Chemistry, 45, 105-123 (1976)

[*]126 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)

a normal (Gaussian) distribution with the median at its peak, as illustrated in Figure 5-12.

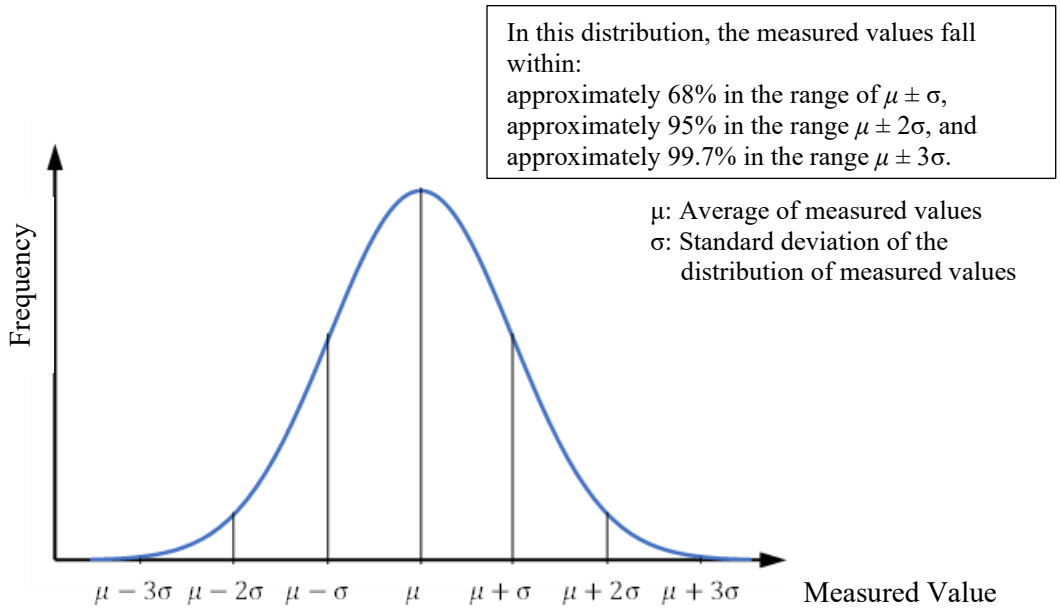


Figure 5-12 Distribution of measured values

Multiple approaches exist for determining the detection limit, and the appropriate method should be selected based on the specific requirements and performance criteria of the survey in which the measurement is conducted. When reporting the lower detection limit, the evaluation method adopted and the associated significance level must be clearly stated. In this measurement method, the Kaiser method and the evaluation method specified in ISO 11929 are described. To date, lower detection limits have often been derived using the Kaiser method, which allows relatively simple calculation based on the sample measurement time, background measurement time, and background counting rate. In recent years, however, from the perspective of harmonization in international comparisons of national metrology standards, general measurement uncertainty in radiation measurements, as well as the related decision threshold and detection limit defined by ISO 11929, have been adopted in evaluations. The calculation method for the lower detection limit for each measurement is selected by the user; however, the method used for evaluation should be explicitly stated as appropriate. For specific calculation methods, refer to Explanation C.

Chapter 6 Quality Assurance

In addition to performing analyses and measurements in accordance with the procedures described in this measurement method, ensuring traceability to national standards and conducting routine inspections to maintain instrument integrity is important. Continuous implementation of these practices makes it possible to demonstrate to third parties that the quality of the analytical results is assured. To ensure analytical quality, it is recommended that the principles of ISO/IEC 17025 be followed. Quality assurance can be broadly divided into internal quality control conducted by analysts themselves and external quality control, such as participation in proficiency testing conducted by external organizations.

6.1 Internal quality control

6.1.1 Traceability

For radiocarbon analysis results, traceability must be ensured for radioactivity (Bq) and mass (kg). For radioactivity, traceability should be ensured for the liquid scintillation counter calibrated using standard sources prepared from standard reference materials, such as those provided by NIST. For mass, traceability should be ensured for the electronic balances used during preparation of measurement samples.

When users prepare efficient sources, they can obtain standard liquid sources traceable to national standards, accompanied by calibration certificates issued by calibration service providers registered under the calibration service provider registration system based on the Measurement Act. For electronic balances, calibration services provided by the manufacturer may be used. Maintenance and inspection, including the issuance of calibration certificates, should be performed.

Equipment calibration should be conducted at appropriate intervals, and calibration validity periods must be established and managed. Within the validity period, it should be confirmed through the routine inspections described in Section 6.1.2 that no changes influencing analytical results have occurred in the instruments.

Traceability should also be ensured for records and other documents associated with analytical results. Specifically, sampling records documenting the sampling date and location, unique identifiers (e.g., analysis numbers) used to identify analytical samples, and various records and forms generated during analytical and measurement operations should be managed in a continuously linked and traceable manner.

6.1.2 Routine inspection

Inspection items and inspection methods for instruments used in radiocarbon analysis and measurement are described below. To determine whether an instrument is in sound condition and suitable for use, acceptable criteria should be established for each inspection item. Provisional criteria may be set based on experimentally obtained initial data and, after sufficient data have

been accumulated, re-established using statistical processing[*127]. Confirmation that no changes affecting analytical results have occurred in the instrument is sufficient; therefore, alternative confirmation methods may also be used. The date of each routine inspection, the responsible person, and the inspection results should be recorded and retained. If routine inspection results indicate that equipment does not meet the acceptable criteria, use of the equipment should be temporarily suspended, the cause investigated, and corrective actions implemented.

If the cause cannot be resolved through re-measurement or reconfiguration by the user, inspection or repair by the manufacturer should be performed.

(1) Liquid scintillation counter

The liquid scintillation counter should be inspected regularly to confirm that no changes influencing analytical results have occurred. The inspection is recommended for each measurement.

・Counting efficiency

A standard source[*128] containing a fixed amount of radioactivity should be measured under identical conditions. If the obtained counts (or count rate) fall within the acceptable criteria, it can be concluded that no change in counting efficiency sufficient to affect the results has occurred. When verifying changes in counting efficiency, the decay of radionuclides contained in the standard source must be taken into account.

・Cooling performance

Liquid scintillation counters equipped with cooling systems maintain a constant temperature inside the measurement chamber. Maintaining a low temperature reduces accidental coincidence counts caused by dark current (dark noise) generated in the photomultiplier tube and suppresses changes in quenching due to temperature fluctuations of the counting samples. A set temperature of approximately 15°C is preferred (refer to the instrument manual and follow the manufacturer's instructions, if specified), with allowable variation within ±3°C.

Using a thermometer with a sensor is convenient for monitoring the temperature inside the measurement chamber. Confirming the temperature without opening the chamber helps suppress temperature fluctuations and reduces the effects of photoluminescence caused by fluorescent or visible light.

・Installation environment

Confirm that the liquid scintillation counter is installed in a location where appropriate air-conditioning control can be maintained and that the installation environment is properly preserved.

---

[*]127 It is convenient to determine the mean and standard deviation and use the range of ±kσ (k = 2 or 3) centered on the mean as the acceptance criterion. In addition, after instrument maintenance or when the lot of emulsifying scintillator changes, it should be considered whether the acceptance criteria require review.

[*]128 The standard source does not need to have the same shape as the measurement container used. Sealed tritium sources supplied with the instrument at delivery may be used. When substituting an unsealed source, such as one used for quenching correction curves, it should be confirmed that no long-term deterioration has occurred by verifying the absence of changes in mass or quenching indicators.

The room temperature should be maintained at approximately 23°C–25°C, with fluctuations within ±2°C, and relative humidity within the range of 30%–80%. Although this does not directly influence analytical quality, liquid scintillation counters with lead shielding are heavy, and it is essential to ensure that the floor load capacity is sufficient to support the instrument weight.

(2) Electronic balance

Electronic balances should be inspected regularly to confirm that no changes affecting analytical results have occurred. Performing pre-use and (post-use) inspections are recommended each time the balance is used, along with periodic inspections approximately once per month.

- Pre-use (post-use) inspection

This inspection is performed before using the balance. Balances with built-in weights should be internally calibrated in advance. Using a calibration weight[*129] close to the mass of the measurement sample (or near the lower limit of the operating range), conduct the pre-use inspection and confirm that the weighing result falls within the acceptable criteria[*130]. Performing the same inspection after use is also desirable.

- Periodic inspections

Check the sensitivity of the balance using a calibration weight with a mass close to the maximum weighing capacity of the electronic balance. Balances with built-in weights should be internally calibrated in advance. The grade of weights used and the acceptance criteria may follow those applied for the pre-use inspection. This inspection should be conducted at regular intervals of approximately once per month.

6.2 External quality control

6.2.1 Interlaboratory comparison

Interlaboratory comparisons using the same sample (preferably ISO/IEC 17025-accredited laboratories) allow verification of the validity of measurement and analysis processes by confirming that no significant differences exist between analytical results.

6.2.2 Proficiency testing

Participation in proficiency testing programs provided by external organizations (preferably ISO/IEC 17043-accredited) enables laboratories to objectively demonstrate competence by comparing analytical results with assigned (reference) values. For proficiency testing under ISO/IEC 17043, methods such as z-scores and En-scores are used to evaluate laboratory performance.

[*]129 Calibration weights with certificates (OIML [JIS] class F2 or higher) are preferred.

[*]130 Acceptance criteria should be determined based on weighing uncertainty, minimum weighing value, and a safety factor. An initial control range of ±0.5% may be adopted (e.g., for a 10 g calibration weight, the acceptable range would be 9.95–10.05 g).

Explanation

Explanation A Specific radioactivity of ^{14}C of NIST oxalic acid

The NIST oxalic acid standard sample used in this measurement method (as of 2023) can be purchased from the U.S. NIST, lot number SRM 4990C. The accompanying certificate does not directly provide the specific radioactivity of ^{14}C, but gives the ratio of radioactivity relative to the older standard SRM 4990 (no longer supplied) as 1.2933 ± 0.0004.

The specific radioactivity of ^{14}C of SRM 4990 is reported as 0.2373 ± 0.0012 Bq/gC (1950)[*131]. Using this value, the specific radioactivity of ^{14}C of SRM 4990C is calculated as:

$$A_{source} = A_0 \times R \times F$$

A_{source}: Specific radioactivity of ^{14}C of SRM 4990C (Bq/gC, as of 2023)

A_0: Specific radioactivity of ^{14}C of SRM 4990 (0.2373 Bq/gC, 1950)

R: Ratio of specific radioactivity of ^{14}C of SRM 4990C to SRM 4990 (= 1.2933)

F: Half-life correction factor (assuming ^{14}C half-life = 5700 years; elapsed time = 73 years from 1950 to 2023[*132])

$$F = \left(\frac{1}{2}\right)^{\frac{(2023-1950)}{5700}} = 0.9912$$

From this,

$$A_{source} = 0.2373 \times 1.2933 \times 0.9912$$
$$= 0.3042$$

Additionally, International Atomic Energy Agency (IAEA)-supplied standard reference materials are also used for quality control of ^{14}C analysis[*133,*134]. Table A.1 lists the recommended specific radioactivity of ^{14}C values for these materials.

[*131] L.M.Cavallo and W.B.Mann : International reference material for contemporary carbon-14 oxalic acid RM-49, National Bureau of Standards Report of Investigation (1980)

[*132] "As of 2023" in the text is an example. The value should be corrected to the time of measurement.

[*133] IAEA reference sheet for quality control materials (2014)

[*134] Rozanski, K. : Consultants' group meeting on ^{14}C reference materials for radiocarbon laboratories. 1991, Internal Report, IAEA, Vienna (1991)

Table A.1 Recommended values of specific radioactivity of ^{14}C for quality control materials

Name	Material	pMC ($^{14}C/^{12}C$) ※			$\delta^{13}C_{PDB}$ (‰)
IAEA-C1	Carbonate	0.00	±	0.02	2.42
IAEA-C2	Carbonate	41.14	±	0.03	-8.25
IAEA-C3	Carbonate	129.41	±	0.06	-24.91
IAEA-C4	Wood	0.20–0.44	±	—	-23.96
IAEA-C5	Wood	23.05	±	0.02	-25.49
IAEA-C6	Sucrose	150.61	±	0.11	-10.8
IAEA-C7	Oxalic acid	49.53	±	0.12	-14.48
IAEA-C8	Oxalic acid	15.03	±	0.17	-18.31
IAEA-C9	Wood	0.12–0.21	±	-	-23.9

※ Refer to Appendix D for conversion from pMC to Bq/gC.

Explanation B Example of uncertainty evaluation

Various approaches to evaluating and expressing the reliability of measurement results have traditionally existed across different countries and technical fields, leading to confusion. In the late 1970s, the International Committee for Weights and Measures brought attention to this issue. This prompted several international metrology organizations to develop a unified approach for consistently assessing and expressing the reliability of measurement results. The outcome of this effort was the Guide to the Expression of Uncertainty in Measurement (GUM), which was published in 1993 jointly by seven international organizations, including ISO. The GUM adopted the position that quantities such as "true value" or "error," which are fundamentally unknowable, should not be introduced into evaluation procedures. To distinguish this position from earlier concepts, a new indicator of measurement reliability, "uncertainty," was introduced to represent measurement reliability. The uncertainty evaluation framework outlined in the GUM has been widely acknowledged for its strong technical rigor and internal consistency. Consequently, the concept of "uncertainty" has been rapidly adopted and is now broadly applied in many fields where it is essential to convey the reliability of measurement results.

In environmental radiation monitoring, measurement results are now widely referenced domestically and internationally, and ensuring traceability to appropriate metrological standards has become increasingly important. Establishing internationally agreed traceability in measurement requires several essential elements, such as an unbroken calibration chain. The evaluation of measurement uncertainty is one of these elements, and calculations and results presentation must be performed according to agreed methods, specifically those based on the aforementioned GUM. Furthermore, participating analytical laboratories must report measurement results with their associated uncertainty in proficiency testing conducted by the IAEA. Thus, using uncertainty as a common international indicator of the reliability of measurement results, international consistency, reliability, and equivalence of results can be ensured. In addition, to demonstrate with high confidence that radioactivity concentrations in environmental samples do not exceed regulatory limits, comparing limit values with upper bounds that consider uncertainty is sometimes necessary.

Measurement uncertainty evaluation has become a widely accepted standard for objectively demonstrating the reliability of environmental radiation monitoring. Adopting this approach would help ensure the credibility and robustness of measurement results for Japanese analytical institutions and related organizations.

This commentary presents procedures for evaluating the uncertainties of individual factors in radiocarbon analysis, with the aim of helping readers understand methods for assessing various sources of uncertainty and enabling individual laboratories to evaluate the uncertainty factors relevant to their work. Estimating uncertainty by considering all possible factors is difficult because there are innumerable potential sources of uncertainty, including those with only minor contributions. Therefore, evaluating every factor is not always necessary in practical operations. Instead, focusing on factors that significantly contribute to the overall uncertainty is more practical.

To assist in identifying such factors, this section provides reference procedures and calculation examples for evaluating uncertainty in actual analytical and measurement processes.

B.1 Basics of uncertainty evaluation

The ultimate measurement target in radionuclide analysis is the radioactivity concentration. However, regardless of how accurately measurements are performed and how thoroughly biases in all measured quantities are corrected, the resulting values remain estimates rather than the true values of the measured quantities themselves. Measurement uncertainty is evaluated as a parameter that expresses the reliability of this estimate. From chemical analysis through radiation measurement, all quantities used as inputs in calculating the radioactivity concentration are also estimates. The measurement uncertainty of the target quantity—the radioactivity concentration—is obtained by combining the uncertainties associated with each of these input values.

The radioactivity concentration is calculated as a function of input values, such as the amount of sample, recovery rate, counting value of radiation emitted by radionuclides in the sample, detector counting efficiency, measurement time, and other correction factors.

$$A = f(x_1, x_2, x_3, \cdots, x_n) \quad \text{(B.1)}$$

A : Radioactivity concentration value

$f(x_1, x_2, x_3, ..., x_n)$: Function used to derive the radioactivity concentration

The combined standard uncertainty of the radioactivity concentration is evaluated by combining the uncertainties of all input quantities involved in its derivation. If each input quantity is independent (i.e., uncorrelated), their uncertainties are combined according to the following equation:

$$u(A) = \sqrt{\sum_{i=1}^{n} \{c_i u(x_i)\}^2} \quad \text{(B. 2)}$$

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

$u(x_i)$: Standard uncertainty of input quantity x_i

c_i : Sensitivity coefficient of the radioactivity concentration value A with respect to the input quantity x_i, given by the differential coefficient $(\partial f/\partial xi)$

In Equation (B.2), ci represents the extent to which radioactivity concentration value A changes in response to a change in each input quantity x_1, x_2, x_3, ..., x_n. For example, the change in A caused by an infinitesimal change Δx_i in the input quantity x_i is given by $(\Delta A) = c_i \Delta x_i$. Accordingly, the change in A that reflects the standard uncertainty of the input quantity x_i is $|c_i|u(x_i)$.

$$f(x_1, x_2, x_3, \cdots, x_n) = \frac{x_1 \cdot x_2 \cdot x_3 \cdot \cdots \cdot x_m}{x_{m+1} \cdot x_{m+2} \cdot x_{m+3} \cdot \cdots \cdot x_n} \quad \text{(B. 3)}$$

Furthermore, if the functional relationship f can be expressed solely as a product and/or quotient of the input quantities x_1, x_2, x_3, ..., x_n (for m < n): then Equation (B.2) is equivalent to the following expression:

$$\frac{u(A)}{A} = \sqrt{\sum_{i=1}^{n} \left\{ \frac{u(x_i)}{x_i} \right\}^2} \qquad \text{(B. 4)}$$

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

$u(x_i)/x_i$: Relative standard uncertainty of the input quantity x_i

Therefore, the relative standard uncertainty of the radioactivity concentration value A can be calculated as the square root of the sum of the squares of the relative standard uncertainties of each input quantity. In practice, Equations (B.2) and (B.4) are used to evaluate measurement uncertainty.

B.2 Uncertainty evaluation procedure

The procedure for evaluating uncertainty is explained below using, as an example, either the analysis of biological samples or that of calcium carbonate by the benzene synthesis method. When radiocarbon is measured using a liquid scintillation counter, the uncertainty associated with the radioactivity concentration expressed per 1 g of carbon in the sample (specific radioactivity of ^{14}C) can be evaluated using the procedure described below.

(1) Identification of uncertainty factors based on the calculation formula for specific radioactivity of ^{14}C (hereinafter referred to as the "model equation")

$$A = \frac{R}{E \times W} \qquad \text{(B. 5)}$$

A : Specific radioactivity of ^{14}C (Bq/gC)
R : ^{14}C count rate (cps)
E : ^{14}C counting efficiency
W : Sample amount (gC)

Various uncertainty factors can be considered for each of these terms. An example of a budget sheet created to organize the uncertainty factors is shown in Table B.1. Notably, factors other than those listed in Table B.1 may also exist and could influence the measurement results.

(2) Evaluation of uncertainty for each individual uncertainty factor.

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

Type A evaluation determines uncertainty by statistically analyzing a series of input values. For each component, the standard uncertainty is taken as the experimental standard deviation derived from repeated measurements.

Type B evaluation assesses uncertainty using methods other than statistical analysis of repeated input values. Each component is evaluated through scientific judgment, drawing on all available information relevant to its possible variation. Such information includes the following:

- Manufacturer's specifications
- Data stated in certificates of calibration and other relevant documents
- Uncertainty assigned to reference data quoted from handbooks
- General knowledge or experience regarding the behavior and characteristics of the relevant materials and measuring instruments

Not all sources of uncertainty contribute significantly to the uncertainty of the measurement result. After the uncertainties from each source are evaluated and combined to determine their contribution to the overall uncertainty, sources with negligible influence may be excluded from further consideration.

(3) Combination of all individual uncertainties to determine the uncertainty of the measurement result.

The relative combined standard uncertainty of the radioactivity concentration is calculated as the square root of the sum of the squares of the relative standard uncertainties of each input quantity.

The combined standard uncertainty of the radioactivity concentration is obtained by multiplying the relative combined standard uncertainty by the radioactivity concentration. The combined standard uncertainty represents the standard deviation associated with the measurement result. When expressing an interval that is expected to include a large proportion of the distribution of values that may reasonably be attributed to the measured value is necessary, the expanded uncertainty is obtained by multiplying the combined standard uncertainty by a coverage factor *k*. The value of *k* is determined based on the applied confidence level and the *t*-distribution[*135], and is generally chosen to be between 2 and 3. In radioactivity concentration measurements, the distribution of measurement results can be regarded as normal; therefore, when the confidence level is approximately 95%, k = 2 is used. When reporting measurement results with their uncertainty, the type of uncertainty is being reported (i.e., whether it is the combined standard uncertainty or the expanded uncertainty [k = 2–3]).

In the calculation example of the relative combined standard uncertainty shown in Table B.1, the overall relative combined standard uncertainty is 1.2% (two significant figures). The breakdown indicates that the majority of the uncertainty arises from three factors: the uncertainty due to the reference standard material (U_2), the uncertainty due to statistical counting during measurement of the standard reference material (U_4), and the uncertainty due to statistical counting during measurement of the sample (U_6). The contributions from other factors are negligible.

This indicates that under analytical and measurement conditions similar to those in the calculation example and for ^{14}C specific activities of the same order or lower, it is practically acceptable to consider only these three factors—namely, the uncertainty due to the reference standard material (U_2), the uncertainty due to statistical counting during measurement of the standard reference material (U_4), and the uncertainty due to statistical counting during measurement of the sample (U_6)—as contributors to the overall relative combined standard uncertainty. The relative combined standard uncertainty is calculated as the square root of the sum of the squares of the relative standard uncertainties of the contributing components. In this process, any component whose contribution is one-tenth or less of the dominant uncertainty has only a minimal effect on the final result and may be omitted for practical purposes. For example, combining a 10% relative standard uncertainty and a 1% relative standard uncertainty yields, $\sqrt{10^2 + 1^2} = 10.05\,\%$ which has minimal effect on the result, as uncertainty is typically expressed with one to two significant figures.

The factors that make substantial contributions to the overall uncertainty must be accurately evaluated in the uncertainty assessment. Attempting to assess every possible factor including those with only minor influence is neither practical nor necessary. In radiation measurements, the uncertainty related to counting statistics and the uncertainty associated with the assigned values of reference sources are the uncertainty factors that contribute most significantly. In most cases, evaluating these factors is sufficient for practical purposes.

---

[*]135 Details are provided in Appendix G of the following document (the t-distribution table is shown in Table G.2 of Annex G). Please use them for reference.
Hidetaka Imai et al.: Guide to the Expression of Uncertainty in Measurement [GUM] Handbook, Japanese Standards Association Publication. ISBN: 9784542307056 (2018)

Notably, not all uncertainty factors listed in Table B.1 need to be evaluated for each measurement. Items that fluctuate with each measurement, such as uncertainty related to counting statistics, must be evaluated every time. However, other items need only be evaluated at specific intervals, such as when equipment is updated, during maintenance inspections, or when reagent lots are changed. In such cases, the relative combined standard uncertainty of a measurement is obtained by combining the uncertainty related to counting statistics (which varies with each measurement) with the other uncertainty factors (which do not vary between measurements).

Table B.1 Uncertainty budget sheet (example)

Uncertainty factor※1	Relative standard Uncertainty	Calculation example※2	Remarks
B.3.1 Sample quantity ($\boldsymbol{W_s}$)	$\frac{\boldsymbol{u(W_s)}}{\boldsymbol{W_s}}$	0.014%	Relative standard uncertainty of (1)
(1) Weighing	$u1$	0.014%	
B.3.2 ^{14}C counting efficiency ($\boldsymbol{\varepsilon}$)	$\frac{\boldsymbol{u(\varepsilon)}}{\boldsymbol{\varepsilon}}$	0.84%	Combined relative standard uncertainty for (1) to (4).
(1) Standard reference sample	u_2	0.49%	
(2) Weighing of standard reference sample	u_3	0.014%	
(3) Counting statistics	u_4	0.68%	
(4) Decay correction	u_5	0.000011%	Negligibly small and does not need to be evaluated
B.3.3 Net ^{14}C count rate ($\boldsymbol{r_n}$)	$\frac{\boldsymbol{u(r_n)}}{\boldsymbol{r_n}}$	0.80%	Combined relative standard uncertainty for (1) to (3).
(1) Counting statistics	u_6	0.79%	Evaluated for each measurement
(2) Variations in measurement system	u_7	0.17%	
(3) Decay correction	u_8	0.000011%	Negligibly small and does not need to be evaluated
Relative combined standard uncertainty※3	$\frac{\boldsymbol{u(A)}}{\boldsymbol{A}}$	1.2%	Evaluated for each measurement

※1 The numbers preceding each uncertainty factor correspond to the sections referenced in B.3.
※2 In this calculation example, intermediate values are shown as rounded values for convenience (calculations are performed without rounding).
※3 The relative combined standard uncertainty should be expressed with no more than two significant figures.

[How to evaluate factors that should be taken into account]

- In this explanation, factors with small contributions are included intentionally to help the reader understand the evaluation process. In practical uncertainty evaluation, priority should be given to: (1) the uncertainty due to counting statistics of the sample measurement (B.3.3(1)); (2) the uncertainty due to counting statistics of the standard reference sample (B.3.2(3)); and (3) the uncertainty of the standard reference sample itself (B.3.2(1)), as these are the main contributors

to overall uncertainty.

- To reliably evaluate uncertainty factors with significant contributions, refer to the factors listed in this table, identify any additional factors likely to have relatively large uncertainties, combine them with the uncertainty from counting statistics, and determine whether they should be included.
- Uncertainty factors not related to counting statistics may be evaluated at appropriate times, such as during instrument replacement, maintenance and inspection, or changes in reagent lots.

B.3 Example of uncertainty calculation procedure

For the example in B.2, the calculation method for each factor listed in Table B.1 is presented for reference.

Note that numerical values are not rounded during the calculation of the uncertainty for each factor; rounding is applied only once, at the final step when determining the relative combined standard uncertainty[*136].

The specific radioactivity of ^{14}C, A (Bq/gC), is obtained from Equation (B.5) using the following measurement model equation:

$$A = \frac{r_n}{\varepsilon \times W_s}$$

A : Specific radioactivity of ^{14}C (Bq/gC)
r_n : ^{14}C count rate (cps)
ε : ^{14}C counting efficiency
W_s : Measured sample amount (gC)

The relative combined standard uncertainty of A is obtained by combining the relative standard uncertainties of each parameter in the measurement model (Ws, ε, and r_n).

Here, the standard uncertainty of A is defined as, $\frac{u(A)}{A}$ and the relative standard uncertainty as u(A)/A. The uncertainties of the other parameters are defined in the same way as.

By applying the relative standard uncertainties of the input quantities x_1, x_2, x_3, ..., x_n defined in Equation (B.4) $\left(\frac{u(x_i)}{x_i}\right)$to each parameter in the measurement model, the relative standard uncertainty of A can be expressed as follows:

$$\frac{u(A)}{A} = \sqrt{\left(\frac{u(W_s)}{W_s}\right)^2 + \left(\frac{u(\varepsilon)}{\varepsilon}\right)^2 + \left(\frac{u(r_n)}{r_n}\right)^2} \qquad \text{(B. 6)}$$

To obtain $\frac{u(A)}{A}$, the relative standard uncertainties of W_s, ε, and r_n are calculated sequentially as described in B.3.1 through B.3.3, and then combined using Equation (B.6) as outlined in B.3.4.

[*136] For clarity in the calculation examples, intermediate values are shown as rounded for presentation purposes; however, all actual calculations are performed without rounding.

B.3.1 Uncertainty of the sample quantity $\left(\frac{u(W_s)}{W_s}\right)$

For biological samples or calcium carbonate, the uncertainty associated with the sample quantity W_s is considered to arise from the uncertainty of weighing. The relative standard uncertainty of the weighing is defined as u_1.

(1) Uncertainty of weighing (u_1)

The method used to determine the uncertainty of depends on whether this uncertainty is stated in the calibration certificate of the electronic balance.

The uneven distribution of radionuclides in the sample may influence the measured value; however, it is difficult to estimate this uncertainty. Accordingly, evaluation of sample homogeneity as part of the uncertainty is not required. Nevertheless, when weighing the sample, it is essential to mix it thoroughly in advance to ensure a homogeneous state.

a) When uncertainty is stated in the calibration certificate

The uncertainty stated in the calibration certificate of the electronic balance is used. If the stated uncertainty is not provided as a relative value, the relative standard uncertainty of weighing (u_1) is calculated using the following equation:

$$u_1 = \frac{u(W_s)}{W_s} \times 100\ (\%) \qquad \text{(B. 7)}$$

$u(W_s)$: Uncertainty of the weighed value (g)

W_s : Weighed value (g)

b) When uncertainty is not stated in the calibration certificate

If the uncertainty is not stated in the calibration certificate of the electronic balance, the relative standard uncertainty of weighing (u_1) is determined by combining the uncertainty due to rounding of the weighing value ($u_{1.1}$) and the uncertainty due to repeatability of weighing ($u_{1.2}$). The combined result represents only the uncertainty at the time of weighing. The measurement uncertainty associated with calibration may be ignored because it is sufficiently small; however, if other significant uncertainty factors exist, they should also be considered.

1) Uncertainty due to rounding of weighing values ($u_{1.1}$)

If the readability limit (minimum scale) of the electronic balance is l, the readings exhibit a rectangular distribution with upper and lower limits of $\pm l/2$ at the zero point and the weighing value. Combining these two distributions results in a triangular distribution with upper and lower bounds of $\pm l$. Therefore, $u_{1.1}$ can be calculated using the following equation:

$$u_{1.1} = \frac{l}{\sqrt{6} \times W_s} \times 100\ (\%) \qquad \text{(B. 8)}$$

l : Readability limit (g)

W_s : Weighed value (g)

2) Uncertainty due to repeatability of weighing ($u_{1.2}$)

Repeat the measurement approximately 10 times using a calibration weight or a similar object with a mass comparable to that of the sample, and calculate the mean value and standard deviation. If the average value of n measurements is used as the sample quantity, $u_{1.2}$ is obtained using the

following equation:

$$u_{1.2} = \frac{W_{STD}}{\overline{W_s}} \times \frac{1}{\sqrt{n}} \times 100\ (\%) \qquad \text{(B. 9)}$$

$\overline{W_s}$: Mean value of repeated measurements (g)

W_{STD} : Standard deviation of repeated measurements (g)

n : Number of measurements of the sample (when the mean value is used as the test portion)

3) Combination of weighing uncertainties

The relative standard uncertainty of weighing, u_1, is obtained by combining $u_{1.1}$ and $u_{1.2}$:

$$u_1 = \sqrt{(u_{1.1})^2 + (u_{1.2})^2} \qquad \text{(B. 10)}$$

[Calculation example]

For an electronic balance with a readability limit of 0.0001 g and a weighing value of 1.7021 g, $u_{1.1}$ is calculated using Equation (B.8) as follows:

$$u_{1.1} = \frac{l}{\sqrt{6} \times W_s} \times 100 = \frac{0.0001}{\sqrt{6} \times 1.7021} \times 100 = 0.0024\ \%$$

When the mean value of repeated measurements is 1.702090 g, the standard deviation is 0.000242 g, and the number of measurements is 1, $u_{1.2}$ is obtained using Equation (B.9) as follows:

$$u_{1.2} = \frac{W_{STD}}{\overline{W_s}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.000242}{1.702090} \times \frac{1}{\sqrt{1}} \times 100 = 0.014\ \%$$

Finally, u_1 is obtained using Equation (B.10) as follows:

$$u_1 = \frac{u(W_s)}{W_s} = \sqrt{(u_{1.1})^2 + (u_{1.2})^2} = \sqrt{0.0024^2 + 0.014^2} = 0.014\ \%$$

B.3.2 Uncertainty of ^{14}C counting efficiency ε, $\left(\frac{u(\varepsilon)}{\varepsilon}\right)$

In radiocarbon measurements, the uncertainty associated with the standard reference material (or standard reference source) used for calibration—namely, the counting efficiency ε—should be considered. Accordingly, $\frac{u(\varepsilon)}{\varepsilon}$ is obtained by combining the following uncertainty components*137: the uncertainty of the standard reference sample (u_2), uncertainty due to weighing of the standard reference sample (u_3), uncertainty due to counting statistics (u_4), and uncertainty due to decay correction (u_5).

(1) Uncertainty of the standard reference sample (u_2)

The uncertainty stated in the certificate of the standard reference material is used.

*137 In the calculation example, uncertainty is determined for the case in which benzene synthesized using NIST oxalic acid (SRM 4990C) and benzene synthesized using marble are measured to calculate the counting efficiency of the sample. For the approach to uncertainty evaluation when preparing a quenching correction curve and using it to determine the sample counting efficiency, refer to The Series of Environmental Radioactivity Measuring Methods No. 9, "Tritium Analysis Methods."

[Calculation example]

When NIST oxalic acid (SRM 4990C) is used as the standard reference sample, the uncertainty of NIST oxalic acid (SRM 4990C) is 0.49%*138.

$u_2 = 0.49\%$

(2) Uncertainty due to weighing of the standard reference sample (u_3)

As with u_1 above, the method for determining the weighing uncertainty depends on whether the uncertainty is stated in the calibration certificate of the electronic balance. If the uncertainty is not stated, the relative standard uncertainty is obtained by combining the relative standard uncertainties due to rounding of the weighing value ($u_{3.1}$) and repeatability of weighing ($u_{3.2}$).

[Calculation example]

For an electronic balance with a readability limit of 0.0001 g and a weighing value of 1.7021 g, $u_{3.1}$ is calculated using Equation (B.8).

$$u_{3.1} = \frac{l}{\sqrt{6} \times W_S} \times 100 = \frac{0.0001}{\sqrt{6} \times 1.7021} \times 100 = 0.0024\ \%$$

When the mean value of repeated measurements is 1.702090 g, the standard deviation is 0.000242 g, and the number of measurements is 1, $u_{3.2}$ is calculated using Equation (B.9).

$$u_{3.2} = \frac{W_{STD}}{\overline{W_S}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.000242}{1.702090} \times \frac{1}{\sqrt{1}} \times 100 = 0.014\ \%$$

Finally, u_3 is obtained using Equation (B.10):

$$u_3 = \frac{u(W_S)}{W_S} = \sqrt{(u_{3.1})^2 + (u_{3.2})^2} = \sqrt{0.0024^2 + 0.014^2} = 0.014\ \%$$

(3) Uncertainty due to counting statistics in standard reference sample measurement (u_4)

The relative standard uncertainty is calculated from the number of counts obtained by measuring the standard reference sample and the statistical uncertainty associated with those counts. If multiple standard reference samples are prepared, the relative standard uncertainty (u_4) is calculated for each sample, and the maximum value (u_{4max}) is used.

$$u_4 = \frac{\sigma}{N} \times 100\ (\%) \qquad (B.11)$$

N : Count obtained using the standard sample

σ : Uncertainty due to counting statistics

[Calculation example]

When the standard reference material measurement yields 21,541 counts and the statistical uncertainty is 146.77 counts, u_4 is calculated using Equation (B.11).

$$u_4 = \frac{\sigma}{N} \times 100 = \frac{146.77}{21541} \times 100 = 0.68\ (\%)$$

*138 Derived from the specific radioactivity of ^{14}C of NIST oxalic acid (SRM 4990C), 0.3042 ± 0.0015 Bq/gC.

(4) Uncertainty due to decay correction (for standard reference sample measurement) (u_5)

Using the nuclear data referenced in the analysis, decay correction factors from the reference date to the measurement date are calculated using the half-life and half-life plus uncertainty. The relative difference between these correction factors is defined as u_5. Because the contribution of uncertainty due to decay correction is negligibly small, it does not need to be evaluated in practical operation.

$$DF_1 = \left(\frac{1}{2}\right)^{\frac{t}{T}} \quad \text{(B. 12)}$$

$$DF_2 = \left(\frac{1}{2}\right)^{\frac{t}{T+\sigma}} \quad \text{(B. 13)}$$

$$u_5 = \frac{|DF_2 - DF_1|}{DF_1} \times 100\ (\%) \quad \text{(B. 14)}$$

DF_1: Decay correction factor at T
DF_2: Decay correction factor at T + σ
t : time
T : Half-life
$T+\sigma$: Half-life plus uncertainty

[Calculation example]

The half-life of ^{14}C is 5,700 years, and the uncertainty of the half-life is 30 years. Using Equations (B.12) to (B.14), and assuming that the measurement is performed 60 days after the reference date, DF_1, DF_2, and u_5 are calculated as follows. The nuclear data used are from ENSDF (Evaluated Nuclear Structure Data File) (as of October 2023). The uncertainty due to decay correction is negligibly small. Moreover, evaluating this source of uncertainty for every measurement sample results in unnecessarily complex calculations; therefore, in practical applications, this factor does not need to be assessed.

$$DF_1 = \left(\frac{1}{2}\right)^{\frac{t}{T}} = \left(\frac{1}{2}\right)^{\frac{(60\div 365.25)}{5700}} = \left(\frac{1}{2}\right)^{\frac{0.16427}{5700}} = 0.99998002$$

$$DF_2 = \left(\frac{1}{2}\right)^{\frac{t}{T+\sigma}} = \left(\frac{1}{2}\right)^{\frac{(60\div 365.25)}{5700+30}} = \left(\frac{1}{2}\right)^{\frac{0.16427}{5730}} = 0.99998013$$

$$u_5 = \frac{|DF_2 - DF_1|}{DF_1} \times 100 = \frac{|0.99998013 - 0.99998002|}{0.99998002} \times 100 = 0.000010\%$$

(5) Combination of uncertainties for ^{14}C counting efficiency ε $\left(\frac{u(\varepsilon)}{\varepsilon}\right)$

$\frac{u(\varepsilon)}{\varepsilon}$ is obtained by combining the uncertainty components u_2 to u_5

$$\frac{u(\varepsilon)}{\varepsilon} = \sqrt{(u_2)^2 + (u_3)^2 + (u_4)^2 + (u_5)^2} \quad \text{(B. 15)}$$

[Calculation example]

The uncertainty components u_2 to u_5 obtained in items (1) to (4) are as follows:

Standard reference sample: $u_2 = 0.49\%$

Weighing of standard reference sample: $u_3 = 0.014\%$

Counting statistics: $u_4 = 0.68\%$

Decay correction: $u_5 = 0.000010\%$

$\frac{u(\varepsilon)}{\varepsilon}$ is obtained by combining these components using Equation (B.15):

$$\frac{u(\varepsilon)}{\varepsilon} = \sqrt{(u_2)^2 + (u_3)^2 + (u_4)^2 + (u_5)^2}$$

$$= \sqrt{0.49^2 + 0.014^2 + 0.68^2 + 0.000010^2}$$

$$= 0.84\%$$

B.3.3 Uncertainty of the net counting rate r_n of ^{14}C $\left(\frac{u(r_n)}{r_n}\right)$

In radiocarbon measurements, the net counting rate r_n is obtained by subtracting the background counting rate from the counting rate of the measured sample, followed by the application of quenching correction and half-life correction to calculate the specific radioactivity of ^{14}C. Thus, the uncertainty $\frac{u(r_n)}{r_n}$ is obtained by combining the relative standard uncertainties due to counting statistics associated with sample measurement (u_6), fluctuations in the measurement system (u_7), and decay correction associated with sample measurement (u_8).

(1) Uncertainty due to counting statistics in sample measurement (u_6)

This uncertainty is calculated in the same manner as u_4 described above. However, the net counting rate of the unknown sample is used in the calculation.

$$u_6 = \frac{\sigma_n}{r_n} \times 100\ (\%) \qquad \text{(B. 16)}$$

r_n : Net count rate of the unknown sample

σ_n : Uncertainty due to counting statistics of the count rate

[Calculation example]

When the sample measurement yields 17,200 counts, the background count is 300 counts, and the measurement time is 60,000 s, the net counting rate is 0.28 ± 0.0022 cps. The uncertainty due to counting statistics, u_6, is calculated using Equation (B.16).

$$u_6 = \frac{\sigma_n}{r_n} \times 100 = \frac{0.0022}{0.28} \times 100 = 0.79\ (\%)$$

(2) Uncertainty due to fluctuations in the measurement system (u_7)

The uncertainty arising from fluctuations in the measurement system can be estimated by assessing the system's stability, that is, by determining an acceptable range of variation.

For example, as part of routine quality control, when measuring a check β-ray source under specified conditions, an allowable range (±R) can be established for fluctuations. The acceptance

criteria may be defined as either the difference between the obtained counting rate and the value stated on the performance certificate falling within a specified range, or the difference between the obtained counting rate and the mean value of the check β-ray source over the past year being within three times the standard deviation. This allowable range can then be used in the calculation of uncertainty. Since u_7 follows a rectangular distribution with limits defined by the allowable fluctuation range, it is calculated using the following equation.

$$u_7 = \frac{R}{\sqrt{3}} \times 100\ (\%) \qquad \text{(B. 17)}$$

R : Upper limit of the allowable range of variation

[Calculation example]

When the allowable fluctuation range determined from check source measurements is ±0.3%, u_7 is calculated using Equation (B.17):

$$u_7 = \frac{R}{\sqrt{3}} \times 100 = \frac{0.003}{\sqrt{3}} \times 100 = 0.17\ \%$$

(3) Uncertainty due to decay correction associated with sample measurement (u_8)

This uncertainty is calculated in the same manner as u_5 described above. Because the contribution of uncertainty due to decay correction is negligibly small, it does not need to be evaluated in practical operation.

[Calculation example]

When the measurement is performed 60 days after sample collection and the specific radioactivity of ^{14}C is calculated, u_8 is obtained using Equations (B.12) to (B.14). Because the contribution of uncertainty due to decay correction is negligibly small, it does not need to be evaluated in practical operation.

$$DF_1 = \left(\frac{1}{2}\right)^{\frac{t}{T}} = \left(\frac{1}{2}\right)^{\frac{(60\div 365.25)}{5700}} = \left(\frac{1}{2}\right)^{\frac{0.16427}{5700}} = 0.99998002$$

$$DF_2 = \left(\frac{1}{2}\right)^{\frac{t}{T+\sigma}} = \left(\frac{1}{2}\right)^{\frac{(60\div 365.25)}{5700+30}} = \left(\frac{1}{2}\right)^{\frac{0.16427}{5730}} = 0.99998013$$

$$u_8 = \frac{|DF_2 - DF_1|}{DF_1} \times 100 = \frac{|0.99998013 - 0.99998002|}{0.99998002} \times 100 = 0.000010\ \%$$

(4) Combination of uncertainties for the net counting rate r_n of ^{14}C $\left(\frac{u(r_n)}{r_n}\right)$

Use the uncertainty components u_6 through u_8 determined in items (1) to (3).

$$\frac{u(r_n)}{r_n} = \sqrt{(u_6)^2 + (u_7)^2 + (u_8)^2} \qquad \text{(B. 18)}$$

[Calculation example]

The uncertainty components u_6, u_7, and u_8 obtained in items (1) to (3) are as follows:

Counting statistics : $u_6 = 0.79\%$

Fluctuations in the measurement system: $u_7 = 0.17\%$

Decay correction : $u_8 = 0.000010\%$

These components are combined using Equation (B.18) to obtain $\left(\frac{u(r_n)}{r_n}\right)$

$$\frac{u(r_n)}{r_n} = \sqrt{(u_6)^2 + (u_7)^2 + (u_8)^2} = \sqrt{0.79^2 + 0.17^2 + 0.000010^2}$$
$$= 0.80\ \%$$

B.3.4 Uncertainty of specific radioactivity A of ^{14}C $\left(\frac{u(A)}{A}\right)$

Using Equation (B.6), the relative standard uncertainties obtained in Sections B.3.1 through B.3.3 are combined to determine $\frac{u(A)}{A}$.

[Calculation example]

The relative standard uncertainties determined in Sections B.3.1 through B.3.3 are as follows:

$$\frac{u(W_s)}{W_s} = 0.014\ \%$$
$$\frac{u(\varepsilon)}{\varepsilon} = 0.84\ \%$$
$$\frac{u(r_n)}{r_n} = 0.80\ \%$$

Using Equation (B.6), these components are combined to obtain $\frac{u(A)}{A}$ (see Table B.1).

$$\frac{u(A)}{A} = \sqrt{\left(\frac{u(W_s)}{W_s}\right)^2 + \left(\frac{u(\varepsilon)}{\varepsilon}\right)^2 + \left(\frac{u(r_n)}{r_n}\right)^2}$$
$$= \sqrt{0.014^2 + 0.84^2 + 0.80^2}$$
$$= 1.2\ \%$$

In the calculation examples presented here, the largest contributors to the overall uncertainty are the uncertainty of the standard reference sample, the counting-statistical uncertainty in the measurement of the standard reference sample, and the counting-statistical uncertainty in the measurement of the sample itself. In measurements of environmental samples, the detected specific radioactivity of ^{14}C is often of a similar magnitude to that in the evaluation example, and in many cases, the contribution of uncertainty due to counting statistics in sample measurement becomes the largest. It is recommended to compare the relative contributions of the individual uncertainty factors and to examine whether the uncertainty associated with dominant factors can be reduced by reviewing and improving the analytical and measurement conditions. In this example, because the uncertainty due to counting statistics contributes the most, the overall uncertainty can be reduced by increasing the measurement time. Although this calculation example for the present measurement method intentionally includes uncertainty components with small contributions to help the reader understand how to evaluate various factors, when performing an actual uncertainty evaluation, it is recommended to prioritize the evaluation of the following three components: uncertainty due to counting statistics in sample measurement, uncertainty due to counting statistics in standard reference sample measurement, and uncertainty of the standard reference sample. Moreover, to reliably evaluate uncertainty factors with significant contributions,

it is advisable to refer to the uncertainties of each factor in this calculation example, identify additional factors likely to introduce large uncertainties, combine these with the statistical uncertainty of the measurements, and then determine whether such uncertainty factors should be taken into account.

Explanation C Examples of activity concentration and lower detection limit calculations

C.1 Specific radioactivity of ^{14}C (Bq/gC) of the sample and uncertainty due to counting statistics associated with the counting rate

The specific radioactivity of ^{14}C of a sample and the uncertainty due to counting statistics associated with the counting rate can be calculated using the following equations:

$$A = \left(\frac{N_s}{t_s} - \frac{N_b}{t_b}\right) \times \frac{1}{\varepsilon} \times \frac{1}{W_S}$$

$$\sigma = \sqrt{\frac{N_s}{{t_s}^2} + \frac{N_b}{{t_b}^2}} \times \frac{1}{\varepsilon} \times \frac{1}{W_S}$$

A : Specific radioactivity of ^{14}C (Bq/gC) of the sample
σ : Uncertainty due to counting statistics
N_s : Number of counts of the measurement sample
t_s : Sample measurement time (s)
N_b : Number of counts of the background measurement sample
t_b : Measurement time for the background (s)
W_S : Amount of carbon in the measured sample (gC)
ε : Counting efficiency for ^{14}C

The measured sample amount W_S can be calculated using the following equation:

$$W_S = W_c \times \frac{72}{78}$$

W_S : Measured sample quantity (gC)
W_c : Mass of benzene used in the measurement (g)

The counting efficiency ε can be calculated as follows:

$$\varepsilon = \left(\frac{N_{source}}{t_{source}} - \frac{N_b}{t_b}\right) \times \frac{1}{W_{source}} \times \frac{1}{0.3042}$$

N_{source} : Number of counts of NIST oxalic acid
t_{source} : Counting time for NIST oxalic acid (s)
W_{source} : Amount of carbon in NIST oxalic acid (gC)
0.3042 : Specific radioactivity of ^{14}C of NIST oxalic acid (SRM 4990C) as of 2023 [*139,*140] (Bq/gC)

*139 "As of 2023" in the text is provided as an example. The value should be corrected to correspond to the time of measurement. Refer to Explanation A for the method used to calculate this value.
*140 If a standard reference material other than SRM 4990C is used, the specific radioactivity of ^{14}C of that standard material should be applied.

C.2 Lower detection limit according to ISO 11929

C.2.1 Concepts

The lower detection limit defined in ISO 11929 incorporates the concepts of Type I and Type II errors for the respective distributions of the background value and the measured value. These concepts are used to establish the decision threshold and detection limit.

Furthermore, ISO 11929 allows for the inclusion of uncertainty in the standard deviation of each distribution. In the Kaiser method, the standard deviation of the measurement-value distribution is represented by the uncertainty arising from counting statistics. In contrast, under ISO 11929, the standard deviation of the distribution is expressed as the combined standard uncertainty of the measurement result, evaluated in accordance with ISO/IEC Guide 98-3:2008, GUM.

C.2.2 Decision threshold

The value A^*, which determines whether a physical effect is present, is defined based on the distribution of blank measurements and is expressed by the following equation:

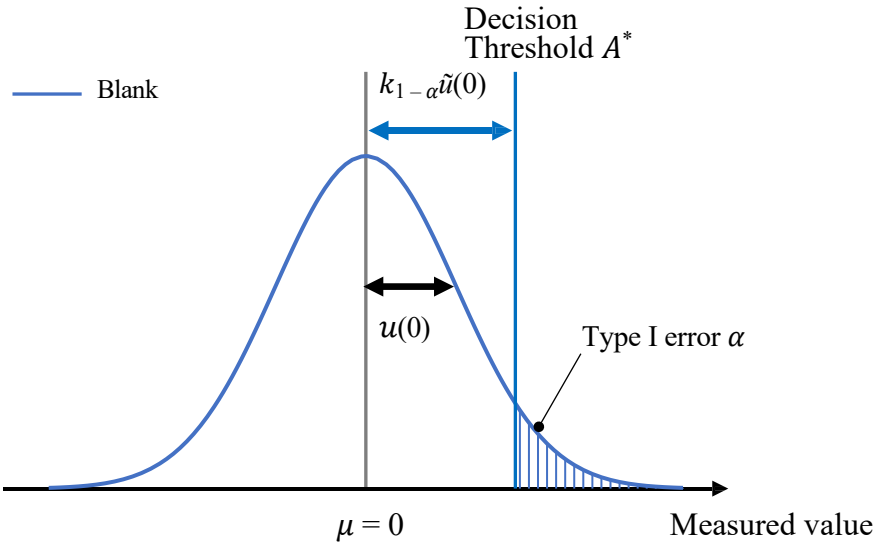
$$A^* = k_{1-\alpha} \times \tilde{u}(0) \qquad \text{(C.1)}$$

Here,

$k_{1-\alpha}$: Coefficient used to avoid a Type I error (i.e., concluding that a physical effect exists when it does not)

$\tilde{u}(0)$: Uncertainty of the measured value when the primary estimate is zero

In a background measurement that contains no radioactive nuclide of interest, the measured values follow a distribution with a mean of $\mu = 0$, as shown in Figure C.1. In this distribution, measured values exceeding the upper limit of the interval corresponding to a confidence level of 1−α (significance level α) are regarded as being significantly different from the blank and are interpreted as indicating the presence of a physical effect. In this case, the probability of a Type I error is α.



$\tilde{u}(0)$: uncertainty of the measured value when the primary estimate is zero
$k_{1-\alpha}$: coefficient used to avoid a Type I error (i.e., concluding that a physical effect exists when it does not)

Figure C.1 Decision threshold

C.2.3 Lower detection limit

The lower detection limit ($A^{\#}$) indicates that the measured value is derived from the sample and not solely from the blank, and it is defined as follows:

$$A^{\#} = A^{*} + k_{1-\beta} \times \tilde{u}(A^{\#}) \qquad \text{(C.2)}$$

Here, $k_{1-\beta}$ is the coefficient used to avoid a Type II error (i.e., concluding that a physical effect does not exist when it actually does), and

$\tilde{u}(A^{\#})$ is the uncertainty of the measurement value when the primary estimate is $A^{\#}$.

In sample measurements, when the primary estimate of the measured value is greater than the decision threshold but close to it, the distribution of measured values overlaps with that of the blank measurements, as shown in Figure C.2.

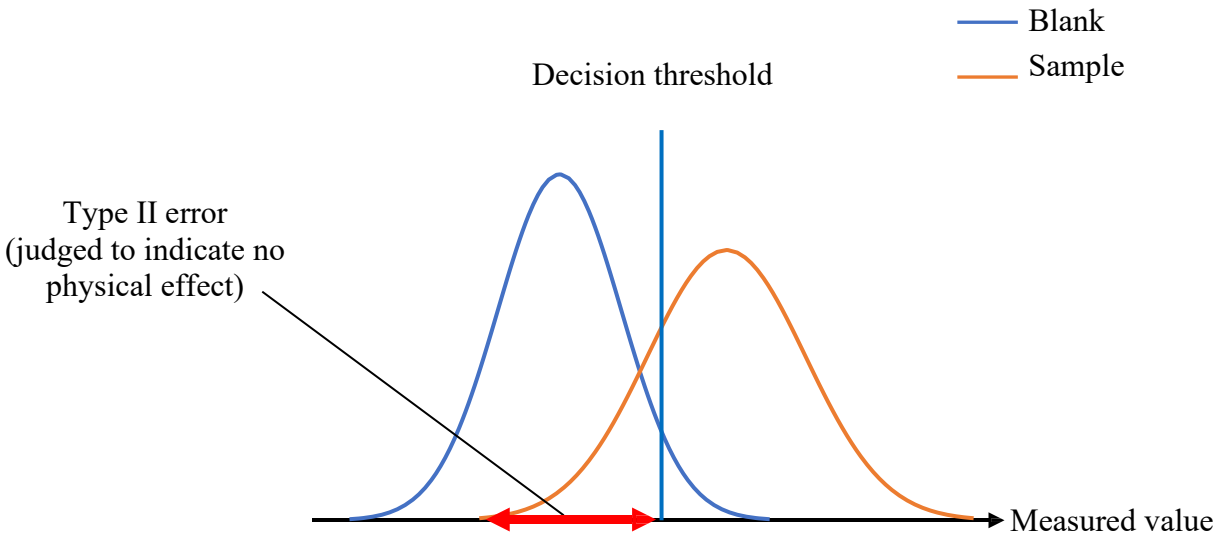
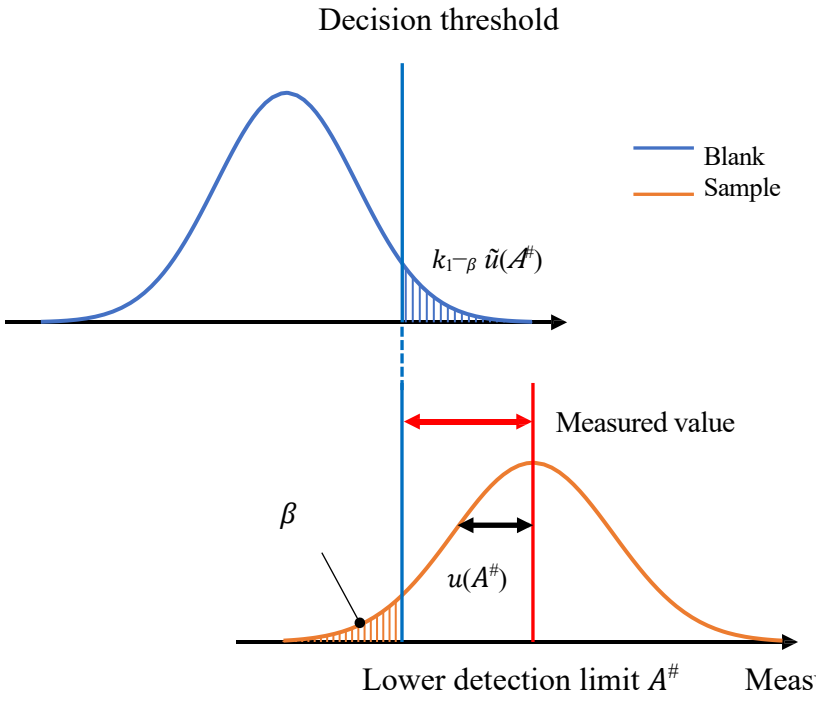


Figure C.2 Distribution of measured values when the primary estimate of the measured value is close to the decision threshold

In this case, measured values falling within the region shown in red in Figure C.2 are below the decision threshold and are therefore judged to indicate no physical effect (Type II error). Accordingly, for the distribution of sample measurements, an interval corresponding to a detection power of $1 - \beta$ is defined. As illustrated in Figure C.3, when the lower bound of this interval coincides with the decision threshold, the corresponding primary estimate of the measured value is defined as the lower detection limit. In this case, the probability of a Type II error is β.



$\tilde{u}(A^{\#})$: the uncertainty of the measurement value when the primary estimate is $A^{\#}$.

$k_{1-\beta}$: coefficient used to avoid a Type II error (i.e., failing to recognize that a physical effect exists)

Figure C.3 Lower detection limit

The lower detection limit is used to evaluate the measurement procedure by comparison with the guideline value Ar. When $A^{\#} < Ar$, the measurement procedure is evaluated as appropriate. When $A^{\#} > Ar$, it is necessary to reduce the lower detection limit, for example, by increasing the measurement time or reviewing the counting conditions. According to ISO 11929-4:2022, the guideline value Ar for general measurements is set to 3 Bq. (for low background counts, 0.1 Bq is specified).

Here, the guideline value Ar, as defined in ISO 11929-1:2019, corresponds to scientific, legal, or other requirements related to detection capability. It serves as a reference value for evaluating measurement procedures through comparison with the lower detection limit.

Note 1: The guideline value may be specified, for example, as radioactivity, specific radioactivity of ^{14}C, activity concentration, activity surface 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 whether it is suitable for the measurement purpose. A measurement procedure meets the requirements when the lower detection limit is smaller than the guideline value.

Note 3: The guideline value should not be confused with other values specified as conformity requirements or regulatory limits.

Figure C.4 summarizes the concepts of the decision threshold and the lower detection limit in a single diagram.

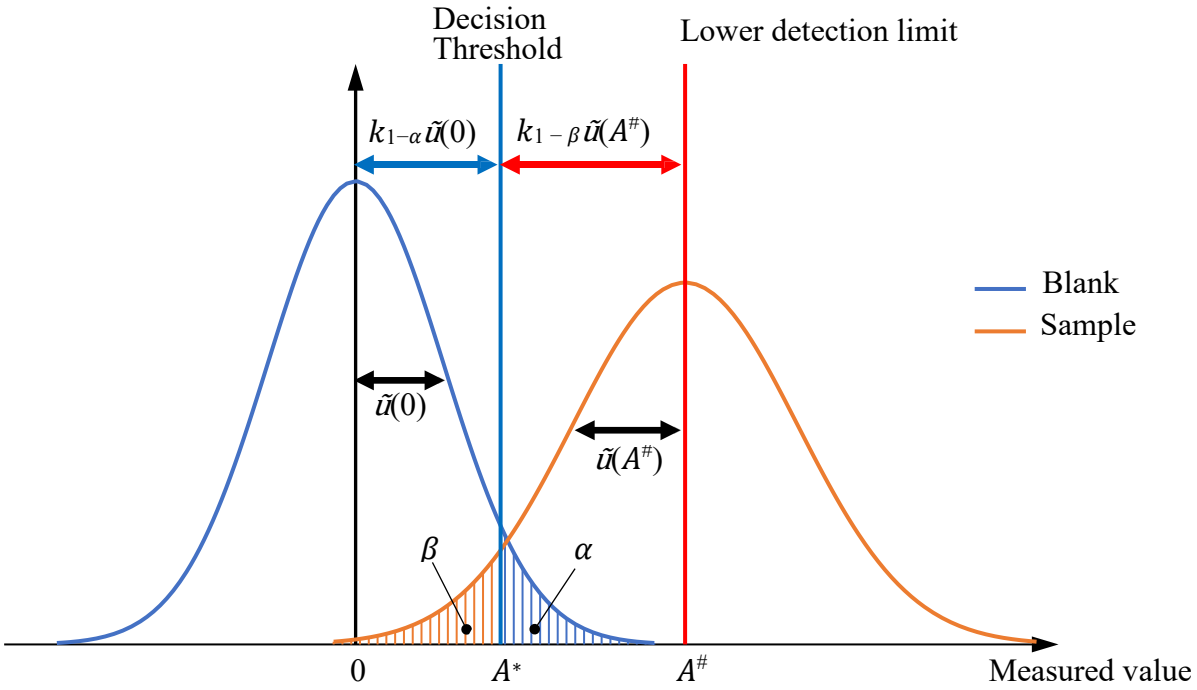


Figure C.4 Concept of the lower detection limit according to ISO 11929

C.2.4 Example of lower detection limit calculation according to ISO 11929

The model equations described in ISO 11929-4[*141] are used to derive the decision threshold and the lower detection limit.

C.2.4.1 General equation for determining radioactivity from measured values

$$A = r_n \cdot w = (r_g - r_0) \cdot w \qquad \text{(C.3)}$$

A : Measured quantity (radioactivity concentration)

r_n : Net counting rate

r_g : Sample counting rate. If the sample count is n_g and the measurement time is t_g, $r_g = n_g/t_g$

r_0 : Denotes the background count rate. If the background count is n_0 and the measurement time is t_0, $r_0 = n_0/t_0$

w : Denotes the conversion factor from counting rate to (specific) radioactivity

$$w = \frac{1}{\varepsilon \cdot W_S \cdot DF}$$

ε : Detection efficiency

W_s : Sample quantity (gC, kg, L, etc.), which is not required when A is expressed as radioactivity

DF : Decay correction factor

If the uncertainties of r_n and w are denoted as $u(r_n)$ and $u(w)$, respectively, the uncertainty of A, u(A), is expressed using the following equation:

$$u(A) = r_n \cdot w \cdot \sqrt{\left(\frac{u(r_n)}{r_n}\right)^2 + \left(\frac{u(w)}{w}\right)^2} \qquad \text{(C. 4)}$$

$$= \sqrt{w^2 u(r_n)^2 + r_n^2\, u(w)^2} \qquad \text{(C. 5)}$$

Furthermore, from Equation (C.3), $r_n = \frac{A}{w}$, and because $u(r_n) = \sqrt{\frac{r_g}{t_g} + \frac{r_0}{t_0}}$ substitution into Equation (C.5) yields the following equation:

$$u(A) = \sqrt{w^2 \left(\frac{r_g}{t_g} + \frac{r_0}{t_0}\right) + A^2 \frac{u(w)^2}{w^2}} \qquad \text{(C. 6)}$$

Here, $u(w)^2/w^2$ represents the relative combined standard uncertainty $u_{rel}(w)$, which includes all uncertainty factors except those related to counting statistics.

[*141] 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)

To calculate the decision threshold and lower detection limit according to ISO 11929, a function of the uncertainty of the measured value, $\tilde{u}(\tilde{A})$, is required, where the variable is the primary estimate $\tilde{A}$ of the measured value. From Equation (C.3), the following equation can be expressed using the first-order estimate $\tilde{a}$:

$$r_g = \frac{\tilde{A}}{w} + r_0 \qquad \text{(C. 7)}$$

Substituting this into Equation (C.6) gives the following equation:

$$\tilde{u}(\tilde{A}) = \sqrt{w^2\left(\left(\frac{\tilde{A}}{w} + r_0\right)/t_g + \frac{r_0}{t_0}\right) + \tilde{A}^2\frac{u^2(w)}{w^2}} \qquad \text{(C. 8)}$$

C.2.4.2 Decision threshold

Substitute the primary estimate $\tilde{A}$ = 0 into Equation (C.8), and then substitute the result, $\tilde{u}(0)$, into Equation (C.1):

$$A^* = k_{1-\alpha} \cdot w \cdot \sqrt{\frac{N_0}{t_0 t_g} + \frac{N_0}{t_0^2}} \qquad \text{(C. 9)}$$

A^* : Decision threshold (Bq or Bq/kg, Bq/L, etc.)

$k_{1-\alpha}$: Coefficient to avoid a Type I error (the error of concluding that something exists when it does not).

C.2.4.3 Lower detection limit

If the lower detection limit is set to $A^{\#}$, substituting $A^{\#}$ into Equation (C.8) and $\tilde{u}(A^{\#})$ in Equation (C.2) yields the following equation:

$$A^{\#} = A^* + k_{1-\beta}\sqrt{w^2\left(\left(\frac{A^{\#}}{w} + r_0\right)/t_g + \frac{r_0}{t_0}\right) + A^{\#2}\frac{u^2(w)}{w^2}}$$

$$(A^{\#} - A^*)^2 = k_{1-\beta}^2\left[w^2\left(\left(\frac{A^{\#}}{w} + r_0\right)/t_g + \frac{r_0}{t_0}\right) + A^{\#2}\frac{u^2(w)}{w^2}\right]$$

$$\left(1 - k_{1-\beta}^2 \times u_{rel}^2(w)\right)A^{\#2} - 2A^*A^{\#} + A^{*2} = k_{1-\beta}^2 w^2\left(\frac{A^{\#}}{wt_g} + \frac{r_0}{t_g} + \frac{r_0}{t_0}\right) \qquad \text{(C. 10)}$$

If we set $k_{1-\alpha} = k_{1-\beta} = k$ here, then, from Equation (C.9), we obtain

$$A^{*2} = k^2 \times w^2\left(\frac{r_0}{t_g} + \frac{r_0}{t_0}\right)$$

Substituting this equation into Equation (C.10) yields

$$\left(1 - k^2 \times u_{rel}^2(w)\right) A^{\#2} - 2A^* A^{\#} + A^{*2} = \frac{k^2 w}{t_g} A^{\#} + A^{*2}$$

$$\left(1 - k^2 \times u_{rel}^2(w)\right) A^{\#2} - \left(2A^* + \frac{k^2 w}{t_g}\right) A^{\#} = 0$$

The lower detection limit can be obtained by solving the quadratic equation.

$$A^{\#} = \frac{2 \times A^* + \frac{(k^2 \times w)}{t_g}}{1 - k^2 \times u_{rel}^2(w)} \qquad \text{(C. 11)}$$

$A^{\#}$: Lower detection limit (Bq or Bq/gC, etc.); and

k : Coverage factor, where

$k = k_{1-\alpha} = k_{1-\beta}$;

$k_{1-\alpha}$: Coefficient to avoid a Type I error (the error of concluding that something exists when it does not)

$k_{1-\beta}$: Coefficient to avoid a Type II error (the error of failing to recognize that something exists when it does)

In general, $\alpha = \beta = 0.05$ (5%), corresponding to a coverage factor of $k_{1-\alpha} = k_{1-\beta} = 1.645$.

$u_{rel}(w)$: Relative standard uncertainty of the conversion factor w
Represents the relative standard uncertainty combining all uncertainties associated with the measurement, excluding those related to counting statistics of the sample measurement.

C.3 Lower detection limit in the Kaiser method

In sample measurements, when the sample contains no radionuclides of interest, the background counting rate follows a distribution shown in Figure C.6. If the counting rate is rn and the uncertainty due to counting statistics is σ, the lower detection limit is defined as the counting rate corresponding to the detectable limit $r_{DL} = k\sigma$.

$$r_{DL} = k\sigma \tag{C.12}$$

Here,

r_{DL} : Counting rate corresponding to the detectable limit

σ : Uncertainty due to counting statistics

k : Coverage factor (often set to 3)

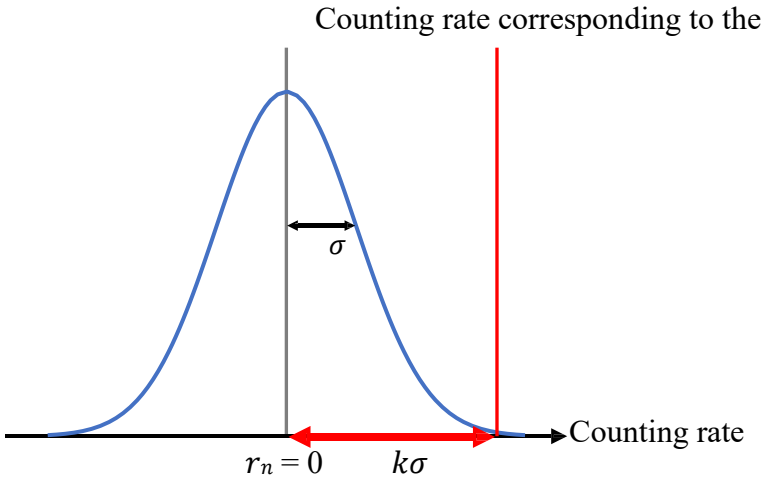


Figure C.6 Conceptual diagram of the lower detection limit in the Kaiser method

Now, define the following.

r_g : Total counting rate of the sample (cps)

r_0 : Background counting rate (cps)

t_g : Sample measurement time (s)

t_0 : Background measurement time (s)

In this case, r_{DL} and σ are expressed as follows:

$$r_{DL} = r_g - r_0 \tag{C. 13}$$

$$\sigma^2 = \frac{r_g}{t_g} + \frac{r_0}{t_0} \tag{C. 14}$$

Substituting Equations (C.13) and (C.14) into Equation (C.12) and solving the quadratic equation for r_{DL} yields the counting rate corresponding to the detectable limit:

$$r_{DL} = \frac{\frac{k^2}{t_g} + k\sqrt{(\frac{k}{t_g})^2 + 4r_0(\frac{1}{t_g} + \frac{1}{t_0})}}{2} \quad \text{(C. 15)}$$

The resulting detectable limit of the counting rate is then converted into activity or activity concentration and used as the lower detection limit.

C.4 Practical calculation example

Measuring conditions:

Sample count value, N_s: 8,500 counts

Sample measurement time, t_s: 500 min (30,000 s)

Background sample count value, N_b: 150 counts

Background measurement time, t_b: 500 min (30,000 s)

Mass of benzene used for measurement, W_c: 1.8000 g

NIST oxalic acid count value, N_{source}: 11,000 counts

NIST oxalic acid counting time, t_{source}: 500 min (30,000 s)

Mass of benzene used for measurement of NIST oxalic acid (SRM 4990C): 1.8000 g

Uncertainty associated with weighing, $u_{rel}(m)$: 0.0024%

Uncertainty associated with instrument calibration, $u_{rel}(cal)$: 0.85%

Uncertainty associated with sample measurement, $u_{rel}(mea)$: 0.17%

C.4.1 Example of calculation of specific radioactivity of ^{14}C and lower detection limit

After calculating the specific radioactivity of ^{14}C, the lower detection limits are calculated using the Kaiser method and ISO 11929.

C.4.1.1 Calculation of specific radioactivity of ^{14}C

1. Determination of the sample quantity W_S (gC)

$$W_S = W_C \times \frac{72}{78}$$
$$= 1.8000 \times \frac{72}{78}$$
$$= 1.6615$$

Similarly, determine the sample quantity in the NIST oxalic acid sample, W_{source} (gC).

$$W_{source} = 1.8000 \times \frac{72}{78} = 1.6615$$

2. Determination of the counting efficiency $\boldsymbol{\varepsilon}$

$$\varepsilon = \left(\frac{N_{source}}{t_{source}} - \frac{N_b}{t_b}\right) \times \frac{1}{W_{source}} \times \frac{1}{A_{source}}$$
$$= \left(\frac{11000}{30000} - \frac{150}{30000}\right) \times \frac{1}{1.6615} \times \frac{1}{0.3042}$$
$$= 0.7156$$

3. Determination of the background counting rate r_0 (cpm) and sample counting rate r_g (cpm)

$$r_0 = \frac{150}{500} = 0.30$$
$$r_g = \frac{8500}{500} = 17.0$$

Thus, the net counting rate r_n (cpm) and its uncertainty $u(r_n)$ (cpm) are:

$$r_n = (r_g - r_0)$$
$$= 17.0 - 0.30$$
$$= 16.7$$

$$u(r_n) = \sqrt{\frac{r_g}{t_g} + \frac{r_0}{t_0}}$$
$$= \sqrt{\frac{17.0}{500} + \frac{0.30}{500}}$$
$$= 0.186$$

4. Determination of the conversion factor w, uncertainty $u(w)$, and relative standard uncertainty $u_{rel}(w)$

$$w = \frac{1}{\varepsilon \cdot W_S}$$
$$= \frac{1}{0.7156 \times 1.6615}$$
$$= 0.8411$$

$$u(w) = w\sqrt{u_{rel}(m)^2 + u_{rel}(cal)^2 + u_{rel}(mea)^2}$$
$$= 0.8411 \times \sqrt{\left(\frac{0.0024}{100}\right)^2 + \left(\frac{0.85}{100}\right)^2 + \left(\frac{0.17}{100}\right)^2}$$
$$= 0.007291$$

$$u_{rel}(w) = \frac{u(w)}{w}$$
$$= 0.008668$$

5. Determination of the specific radioactivity A of ^{14}C (Bq/gC) and the combined standard uncertainty $u(A)$

$$A = \frac{r_n \times w}{60}$$
$$= \frac{16.7 \times 0.8411}{60}$$
$$= 0.234$$

$$u(A) = A \times \sqrt{\left(\frac{u(r_n)}{r_n}\right)^2 + \left(\frac{u(w)}{w}\right)^2}$$
$$= 0.234 \times \sqrt{\left(\frac{0.186}{16.7}\right)^2 + \left(\frac{0.007291}{0.8411}\right)^2}$$
$$= 0.0033$$

C.4.1.2 Calculation of the lower detection limit using the Kaiser method

1. Determination of the lower detection limit using the Kaiser method The counting rate corresponding to the detectable limit, r_{DL} (cpm), is obtained using Equation (C.15).

$$r_{DL} = \frac{\frac{k^2}{t_g} + k\sqrt{(\frac{k}{t_g})^2 + 4r_0(\frac{1}{t_g} + \frac{1}{t_0})}}{2}$$
$$= \frac{\frac{3^2}{500} + 3\sqrt{(\frac{3}{500})^2 + 4 \times 0.30 \times (\frac{1}{500} + \frac{1}{500})}}{2}$$
$$= 0.1133$$

2. The obtained counting rate is converted to specific radioactivity of ^{14}C using the sample quantity, counting efficiency, and related parameters to determine the lower detection limit $A^{\#}_{Kaiser}$ (Bq/gC).

$$A^{\#}_{Kaiser} = \frac{r_{DL}}{W_S \times \boldsymbol{\varepsilon} \times 60}$$
$$= \frac{0.1133}{1.6615 \times 0.71554 \times 60}$$
$$= 0.00159$$

C.4.1.3 Calculation of the lower detection limit based on ISO 11929

1. Determination of the decision threshold from (C.9)

$$A^* = k_{1-\alpha} \cdot w \cdot \sqrt{\frac{n_0}{t_0 t_g} + \frac{n_0}{t_0^2}}$$
$$= 1.645 \cdot 0.8412 \cdot \sqrt{\frac{150}{(500 \times 60) \times (500 \times 60)} + \frac{150}{(500 \times 60)^2}}$$
$$= 0.00080$$

2. Using the obtained decision threshold, calculate the lower limit value from Equation (C.11)

$$A^{\#}_{ISO11929} = \frac{2 \cdot A^{*} + \frac{k^2 \cdot w}{t_g}}{1 - k^2 \cdot u_{rel}(w)^2}$$

$$= \frac{2 \cdot 0.00080 + \frac{1.645^2 \cdot 0.8411}{500 \times 60}}{1 - 1.645^2 \cdot 0.008668^2}$$

$$= 0.00167$$

The above results are summarized in Table C.1. No half-life correction was performed.

Table C.1 Lower detection limits for each parameter obtained by each calculation method

Parameter	Kaiser method	ISO 11929
Specific radioactivity A of ^{14}C (Bq/gC)	0.234	
Combined standard uncertainty $u(A)$(Bq/gC)	0.0033	
Decision threshold A^{*} (Bq/gC)	0.00159	0.00080
Lower detection limit $A^{\#}$ (Bq/gC)		0.00167

C.4.2 Calculation of specific radioactivity of ^{14}C without using uncertainty

Even when uncertainty has not been evaluated, the specific radioactivity of ^{14}C and the counting error can be calculated using the procedure described in Section C.1.

1. Determination of the mass of benzene used in the measurement

The mass of the benzene, W_S (gC), used in the measurement is determined as follows:

$$W_S = W_C \times \frac{72}{78}$$

$$= 1.8 \times \frac{72}{78}$$

$$= 1.6615$$

Similarly, the mass of NIST oxalic acid W_{source} (gC) is determined as follows:

$$W_{source} = 1.8 \times \frac{72}{78} = 1.6615$$

2. Determination of the counting efficiency ε (%)

$$\varepsilon = \left(\frac{N_{source}}{t_{source}} - \frac{N_b}{t_b}\right) \times \frac{1}{W_{source}} \times \frac{1}{0.3042}$$

$$= \left(\frac{11000}{30000} - \frac{150}{30000}\right) \times \frac{1}{1.6615} \times \frac{1}{0.3042}$$

$$= 0.7156$$

3. Determination of the specific radioactivity of ^{14}C of the sample (Bq/gC)

$$A = \left(\frac{N_s}{t_s} - \frac{N_b}{t_b}\right) \times \frac{1}{\varepsilon} \times \frac{1}{W_S}$$
$$= \left(\frac{8500}{30000} - \frac{150}{30000}\right) \times \frac{1}{0.7156} \times \frac{1}{1.6615}$$
$$= 0.234$$

4. Determination of the counting error

$$\sigma = \sqrt{\frac{N_s}{{t_s}^2} + \frac{N_b}{{t_b}^2}} \times \frac{1}{\varepsilon} \times \frac{1}{W_S}$$
$$= \sqrt{\frac{8500}{30000^2} + \frac{150}{30000^2}} \times \frac{1}{0.7155} \times \frac{1}{1.6615}$$
$$= 0.0026$$

Information

Information A Accelerator mass spectrometry

Radioactivity measurement using liquid scintillation counting with the benzene synthesis method has traditionally been used for the measurement of ^{14}C. However, this method requires large sample amounts and time-consuming pretreatment procedures. Accelerator mass spectrometry (AMS) is a technique that overcomes these drawbacks.

Accelerator mass spectrometry is an analytical method that combines the principles of particle accelerators and mass spectrometry[*142]. It is an ultra-sensitive analytical technique designed to determine trace amounts of long-lived radionuclides (e.g., ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, and ^{129}I)[*143]. Because AMS can process trace isotopes contained in a sample and measure isotope ratios with extremely high sensitivity, it enables the detection of radionuclides with very low natural abundances. By physicochemically separating isotopes contained in a sample and directly counting individual atoms, AMS allows measurements to be performed using sample amounts less than one-thousandth of those required for conventional analytical methods[*144], while also enabling much shorter measurement times. Based on this principle, the number of atoms of long-lived radionuclides can be determined directly. Currently, this technique is widely applied not only to environmental radioactivity analysis but also to many other fields, such as radiocarbon dating[*145], and is regarded as an alternative analytical method to radiation measurement. However, AMS instruments are extremely large and expensive, and their operation and maintenance involve substantial costs. From the viewpoint of cost-effectiveness, application to routine environmental monitoring around nuclear facilities is therefore considered difficult. In Japan, facilities possessing AMS instruments are limited to those listed in Table A.1.

Table A.1 Facilities in Japan performing AMS analysis (as of 2023)

Location	Accelerator	Analyzed nuclides (including those under consideration)
Japan Atomic Energy Agency (Aomori Research and Development Center)	Tandetron (3 MV)	^{14}C,^{129}I
Yamagata University (Center for Accelerator Mass Spectrometry)	Tandem (500 kV)	^{14}C
Institute of Accelerator Analysis Ltd.	Tandem (3 MV, 500 kV)	^{14}C
Paleo Labo Co., Ltd.	Tandem (500 kV)	^{14}C

*142 松崎浩之：加速器質量分析の原理, Journal of the Vacuum Society of Japan, 50(7), 467-474 (2007)

*143 Saito-Kokubu, Y., Matsubara, A., Fujita, N., Kuwabara, J., & Kinoshita, N.：JAEA-AMS-TONO 及び JAEA-AMS-MUTSU 間での炭素同位体標準試料測定の比較試験結果.,JAEA Technology (2022)

*144 小田寛貴, 中村俊夫, & 古川路明：名古屋大学タンデトロン加速器質量分析計による古文書資料の ^{14}C 年代測定, 名古屋大学加速器質量分析計業績報告書, IX, 324-334(1998)

*145 中村俊夫：加速器質量分析 (AMS) 法による^{14}C 年代測定の高精度化及び正確度向上の検討, 第四紀研究, 34(3), 171-183 (1995)

National Institute for Environmental Studies	Tandem (3 MV, 500 kV)	^{14}C,^{129}I
University of Tsukuba (Center for Reserch in Radiation, Isotopes, and Earth System Sciences)	Tandem (6 MV)	^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, ^{41}Ca, ^{90}Sr, ^{129}I
The University of Tokyo (The University Museum)	Tandem (5 MV, 500 kV)	^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, ^{41}Ca, ^{90}Sr, ^{129}I, ^{236}U
The University of Tokyo (Atmosphere and Ocean Research Institute)	SSAMS (250 kV)	^{14}C
Japan Atomic Energy Agency (Tono Geoscience Center)	Tandem (5 MV, HVE 330 kV)	^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, ^{41}Ca, ^{90}Sr, ^{129}I
Nagoya University (Institute for Space–Earth Environmental Research)	Tandem (3 MV)	^{14}C

A.1 Preparation of measurement samples

A.1.1 Standard samples

During each sample measurement, international reference standard samples supplied by the IAEA and NIST are measured simultaneously as indicators for verifying the accuracy of isotope ratios. For details on reference standard samples, refer to "Explanation A: Specific Radioactivity of ^{14}C of NIST oxalic acid."

A.1.2 Preparation and handling of measurement samples

In AMS, solid carbon (hereinafter referred to as graphite) is used as the measurement sample. Therefore, after removing impurities from the sample through chemical pretreatment, the carbon contained in the sample must be extracted as CO_2 and subsequently reduced to prepare graphite. A brief description of CO_2 production, purification, and graphitization for each sample type is presented below[*146,*147].

A.1.2.1 Production of CO_2

The method for producing CO_2 is selected according to the sample type.

(1) Atmospheric samples

For atmospheric samples, CO_2 in air is collected in the form of carbonate and then decomposed with phosphoric acid in a vacuum line to release CO_2 (phosphoric acid method). For details of air sampling procedures, refer to "Chapter 1 Atmosphere," Section 1.2, "Sample Collection Methods."

*146 Saito-Kokubu, Y., Matsubara, A., Fujita, N., Kuwabara, J., & Kinoshita, N.：JAEA-AMS-TONO 及び JAEA-AMS-MUTSU 間での炭素同位体標準試料測定の比較試験結果.,JAEA Technology (2022)

*147 北川浩之, 中村俊夫, & 福沢仁之：水月湖湖底・年縞堆積物の AMS-^{14}C 年代, 名古屋大学加速器質量分析計業績報告書, VI, 27-42 (1995)

(2) Water samples

For water samples, such as seawater, concentrated phosphoric acid is added to the sample in a vacuum line to produce CO_2. The solution is bubbled with nitrogen gas to extract the CO_2.

(3) Soil samples

Soil samples are treated with hydrochloric acid to remove carbonates and soluble components, thoroughly rinsed with distilled water, and dried. The dried samples are then combusted with copper oxide (CuO) to oxidize the carbon and produce CO_2 (combustion method).

(4) Biological samples

Biological samples, such as vegetables, are thoroughly dried and pulverized.

The powdered sample is combusted with copper oxide (CuO) to oxidize the carbon and produce CO_2 (combustion method).

For biological samples with high oil content, such as marine organisms, the sample is first converted to a carbonate form, similar to atmospheric samples, and then decomposed with phosphoric acid to release CO_2 (phosphoric acid method).

A.1.2.2 Purification of CO_2

Because the CO_2 gas collected in A.1.2.1 contains water and other gases, excess water and gases are removed in a vacuum line, and only CO_2 is purified.

A.1.2.3 Production of graphite

The purified CO_2 gas is mixed with iron powder as a catalyst and hydrogen gas, and the mixture is heated in an electric furnace to produce graphite. The resulting graphite is wrapped in heat-sterilized aluminum foil or a similar material and submitted to the analytical facility as a target for measurement.

A.2 Measurements and calculations

A.2.1 Measurement system

In AMS, the accelerator plays a key role in separating ions and nuclides. Typically, an electrostatic accelerator, such as a tandem accelerator (Tandetron or Pelletron), is used (see Figure A.1). This accelerator performs two-stage acceleration of negative and positive ions. The system consists of (1) an ion source, (2) an accelerator, and (3) a detector unit. Using this analytical system, the ratio of ^{14}C to ^{13}C ($^{14}C/^{13}C$) in a carbon sample is measured[*148].

A.2.2 Conversion to specific radioactivity of ^{14}C (Bq/gC)

Data obtained by accelerator mass spectrometry are generally expressed in units of pMC

[*148] Saito-Kokubu, Y., Matsubara, A., Fujita, N., Kuwabara, J., & Kinoshita, N.：JAEA-AMS-TONO 及び JAEA-AMS-MUTSU 間での炭素同位体標準試料測定の比較試験結果.,JAEA Technology (2022)

(percent modern carbon), which represent the radioactivity concentration of ^{14}C. The formula for converting the measurement results to specific radioactivity of ^{14}C (Bq/gC) is shown below*[149].

$$\text{Specific radioactivity of } ^{14}C \text{ (Bq/gC)} = 13.56 \times \text{pMC}/100/60$$
$$= \text{pMC} \times 0.00226$$

*149 See Appendix D for details.

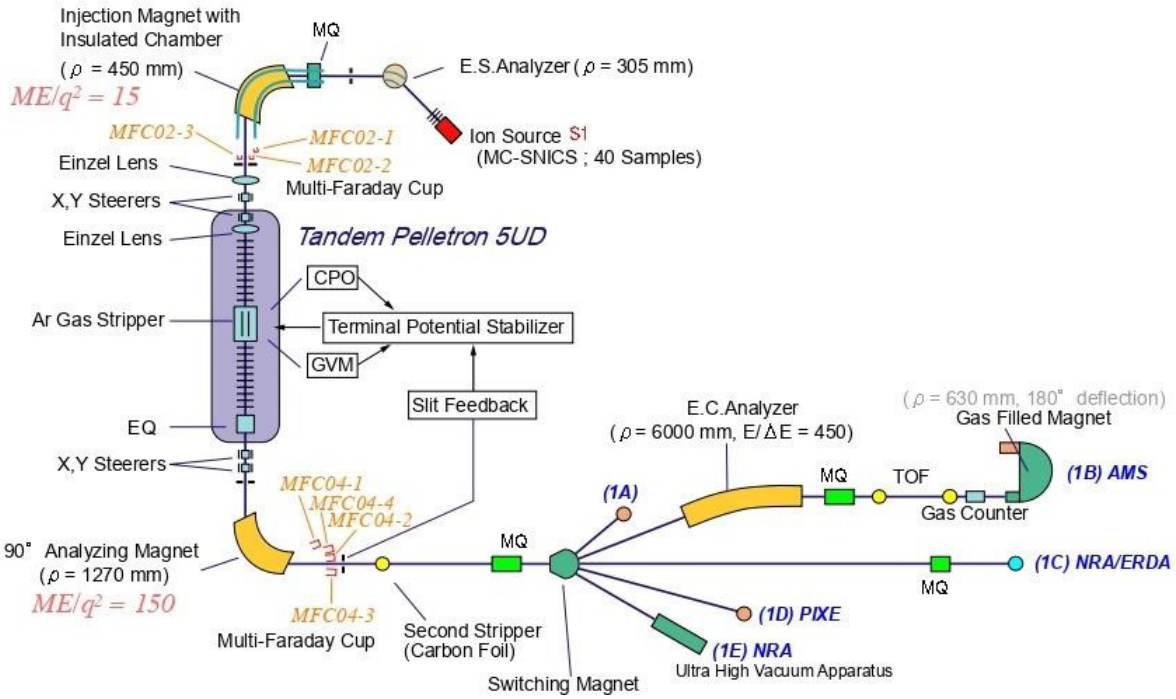


Figure A.1 Overall beamline layout of the accelerator mass spectrometry (AMS) system owned by the University of Tokyo (The University Museum)[*150]

[*150] 松崎浩之. (2020, February). 東大 MALT における加速器ビーム分析システムの現状. 応用物理学会学術講演会講演予稿集 第 67 回応用物理学会春季学術講演会 (pp. 591-591). 公益社団法人 応用物理学会.

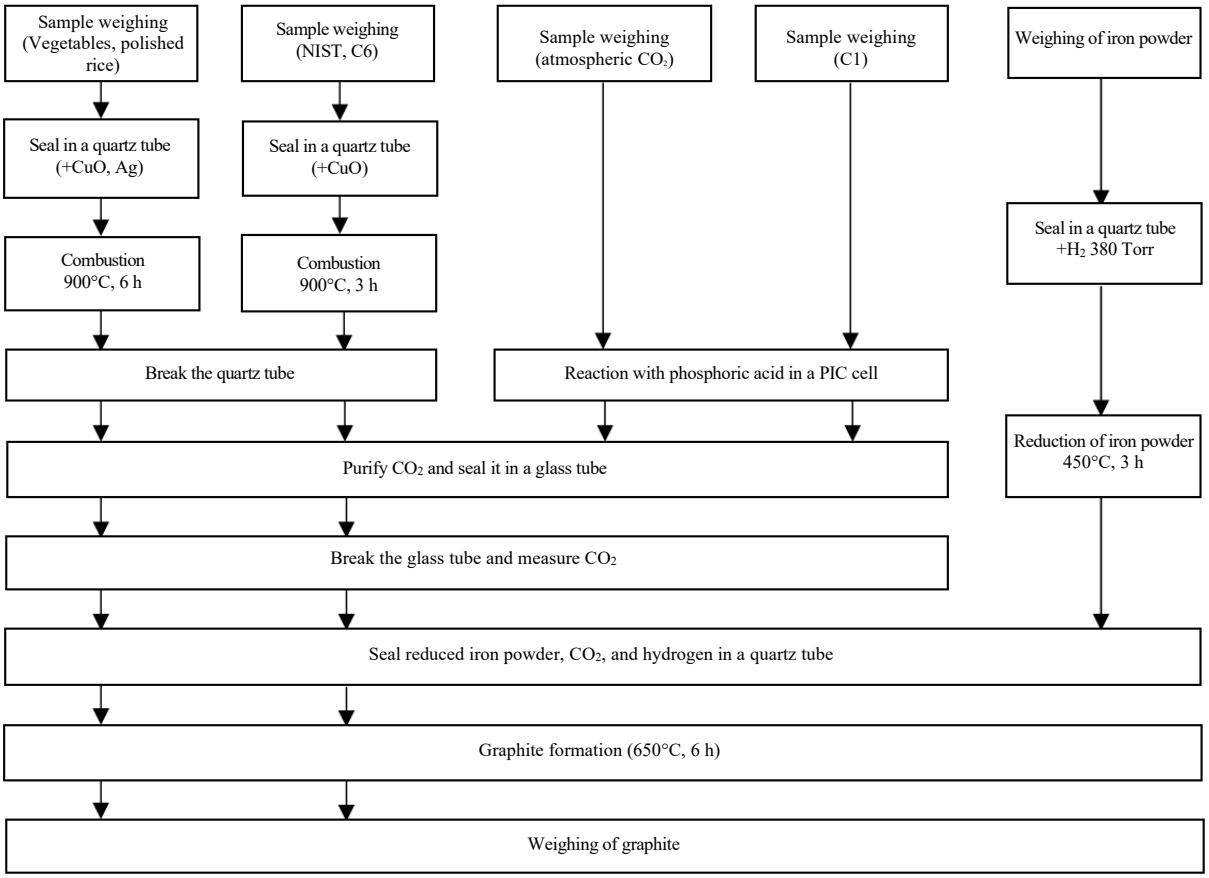


Figure A.2 AMS pretreatment flowchart[*151][*152]

[*151] This refers to international standard samples supplied by the IAEA and the National Institute of Standards and Technology (NIST) (see Explanation A: NIST Carbon-14 Concentration of Oxalic Acid).

[*152] The pressure unit most commonly used in analytical methods is Torr (mmHg). The relationship with Pa (pascal), which is used in the International System of Units (SI), is shown below:
1 Torr = 1 mmHg = 1.333×10^2 Pa

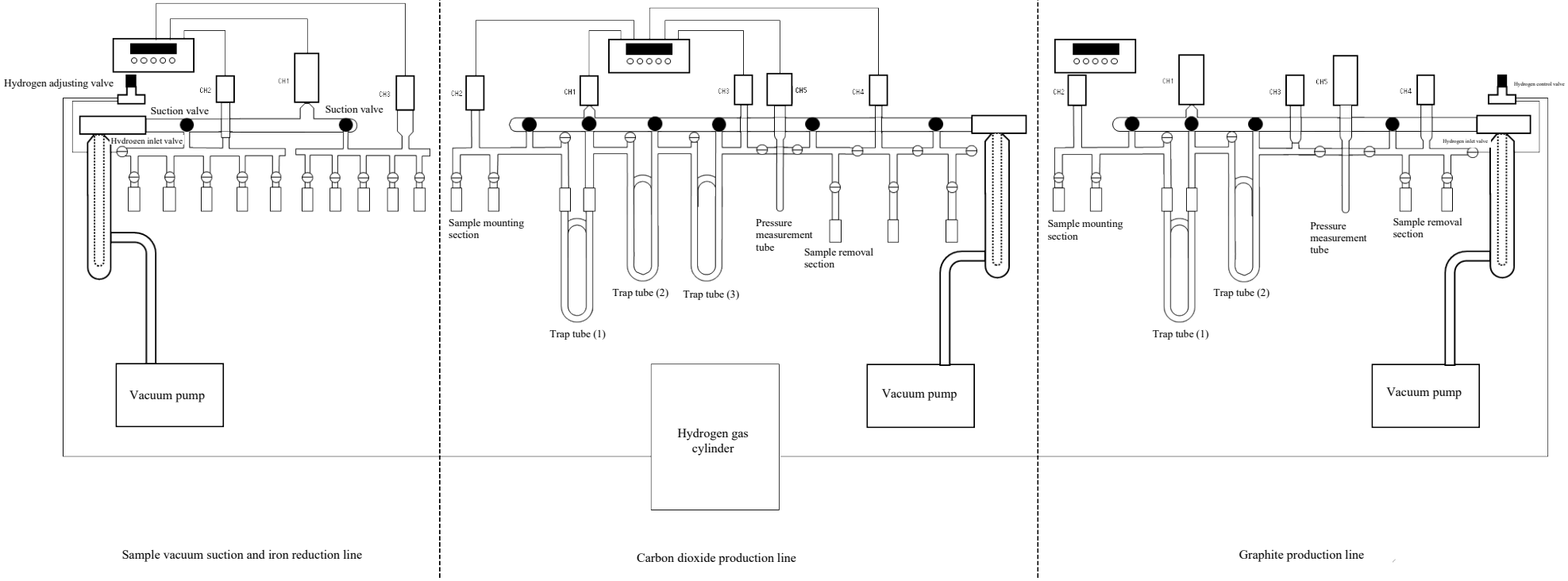


Figure A.3 AMS vacuum-line pretreatment system

Appendix

Appendix A Nuclear data

Nuclear data used for radioactivity calculations should be obtained from a reliable nuclear data compilation. Nuclear data must be preferably included with the analysis results. As an example of a nuclear data compilation, refer to The Series of Environmental Radioactivity Measuring Methods No. 7, "Gamma-ray Spectrometry Using a Germanium Semiconductor Detector," Chapter 6, "Nuclear Data."

In the present measurement method, nuclear data for ^{14}C obtained from Evaluated Nuclear Structure Data File (ENSDF), which is managed by the U.S. National Nuclear Data Center (NNDC), are shown in Table A.1. The decay scheme of ^{14}C is shown in Figure A.1.

Table A.1 ^{14}C nuclear data

Half-life (years)	Maximum β-ray energy (keV)	Decay mode (emission ratio, %)
5700 ± 30	156.475 ± 0.004	β^- (100)

※1 The source of the nuclear data is ENSDF (as of October 2023).
※2 The half-life and maximum β-ray energy are provided together with their uncertainties.

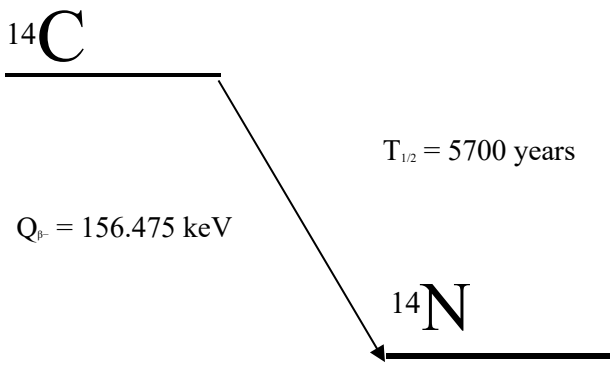


Figure A.1 Decay scheme of ^{14}C

Appendix B Terminology

Term	Description
Primary estimate	An estimate calculated mathematically as the statistically most probable value. This value is referred to as a “primary estimate” in ISO 11929.
Quenching	The quenching effect is a reduction in scintillation light output caused by various factors. Types include chemical quenching, color quenching, oxygen quenching, and concentration quenching.
Counting rate	The number of counts per unit time, usually expressed as counts per minute (cpm) or counts per second (cps).
Decision threshold	In the calculation of detection limits according to ISO 11929, the boundary value of the background distribution corresponding to a probability α of a Type 1 error (incorrectly judging that a physical effect is present in background measurements).
Lower detection limit	The minimum detectable quantity. Methods for calculating the lower detection limit include the Kaiser method, ISO 11929, and the Cooper method.
Quartz wool	A fibrous material made from quartz glass. It has excellent chemical resistance and heat resistance.
Low-potassium glass	Glass with a low potassium content. It exhibits a low background count in liquid scintillation counting.
Half-life	The time required for radioactivity to decrease to one-half of its value at a given reference time. The half-life is intrinsic to each radionuclide and ranges from far less than one second to several billion years. If the half-life is denoted as T, the radioactivity at the reference time (t = 0) is A_0, and the time elapsed from the reference time is t, the radioactivity A at time t can be expressed as follows: $A = A_0 e^{-\lambda t}$ or $A = A_0(\frac{1}{2})^{t/T}$. The relationship between T and the decay constant (λ) is $T = \frac{ln\,2}{\lambda}$, where ln is the natural logarithm (ln 2 = 0.693).
Pirani vacuum gauge	An electrical resistance–type vacuum gauge. Its typical measurement range is 0.4–2000 Pa, allowing measurement at lower pressures than digital manometers. A filament inside the sensor is heated by an electric current. When gas comes into contact with the filament, its temperature decreases. The pressure is calculated from changes in resistance or from the power required to maintain a constant filament temperature.

Uncertainty	The range of variation that a measured result may statistically take. It is obtained by combining uncertainties associated with counting statistics (conventionally called counting error), measurement efficiency, and the weighing of samples used in the analysis. However, uncertainties that are negligibly small do not need to be included.
Saturated solution	A solution in which the maximum amount of solute has been dissolved in a solvent at a given temperature, such that no additional solute can dissolve.
Digital manometer	A pressure gauge suitable for measuring higher pressures than a Pirani gauge. It uses a thin membrane with embedded piezoresistive elements. A difference in pressure on either side of the membrane causes deflection, which changes the resistance of the piezoresistive elements and, in turn, the voltage, allowing measurement of the differential pressure.
^{14}C	A radioactive isotope of carbon with a mass number of 14. It has a half-life of 5700 years and is a β-ray-emitting radionuclide with a maximum β-ray energy of 156 keV.
En score	One of the methods used to evaluate the performance of a testing laboratory. It is expressed by the following equation. An absolute value of ≤1 indicates satisfactory performance. $$En = \frac{\text{Analytical value}_{\text{lab}} - \text{Analytical value}_{\text{ref}}}{\sqrt{{U_{lab}}^2 + {U_{ref}}^2}}$$ Here, U_{lab} is the expanded uncertainty of the participating laboratory (coverage factor k = 2) and U_{ref} is the expanded uncertainty of the reference laboratory or assigned value (k = 2).
w/v%	Mass percentage concentration

Appendix C Results of cross-check between analytical methods

A cross-check was conducted by measuring radiocarbon in rice, sugar, powdered milk, and surimi (fish paste) using four different analytical methods, with the participation of five analytical institutions[*153].

1. Preparation of samples

(1) Rice: Two kilograms of commercially available, standard-grade rice were thoroughly mixed and used as the analytical sample.

(2) Sugar: Two kilograms of commercially available granulated sugar were thoroughly mixed and used as the analytical sample.

(3) Powdered milk: One kilogram of commercially available infant dry milk was thoroughly mixed and used as the analytical sample.

(4) Surimi: Two kilograms of surimi (a raw material for fish paste kamaboko) were homogenized using a mixer and freeze-dried. The resulting dried material was pulverized, mixed, and combusted in an oxygen stream. The produced carbon dioxide was absorbed in aqueous ammonia, calcium chloride was added to precipitate calcium carbonate, and the precipitate was dried and used as the analytical sample.

2. Homogeneity test results

(1) Method

The weight of the sample subjected to combustion was varied over a range of approximately 0–20 g, and the amount of recovered carbon was measured to confirm that a proportional relationship existed between the two.

(2) Result

It was confirmed that the combustion weight and the amount of recovered carbon were approximately proportional. The amount of recovered carbon (g) per gram of combustion sample weight (g) for each sample is shown below.

Sample	Rice	Sugar	Powdered milk	Surimi
Recovered carbon (g)	0.35	0.40	0.48	0.43

3. Analytical methods used in the cross-check

Benzene synthesis method: Three institutions
Accelerator mass spectrometry: One institution
CO_2 absorption method: One institution
Gas counting method[*154]: One institution

4. Result

The results of the cross-check are shown in Table C.1.

[*153] One institution performed the analysis using two different methods.

[*154] The gas counting method involves filling a counter tube with a carbonic acid gas (such as carbon dioxide, methane, or acetylene) obtained from a sample and measuring its radioactivity by passing an electric current through it. This measurement method is not included in this document.

Table C.1 Cross-check results

(Unit: Bq/gC)

Sample	Rice	Sugar	Powdered milk	Surimi
Mean value	0.258	0.262	0.251	0.238
Standard deviation (σ_{n-1})	0.0053	0.0046	0.014	0.0051
Coefficient of variation (%)	2.1	1.8	5.8	2.2

※The number of data points is 6.

※Samples were collected around 1990.

Appendix D Units and isotopic fractionation effects

There are several ways to express radiocarbon quantities. In environmental measurements, ^{14}C radioactivity concentrations are commonly expressed as specific radioactivity of ^{14}C (Bq/gC) or radioactivity concentration (Bq/m^3, Bq/L, etc.). Radiocarbon levels may also be expressed as relative concentrations with respect to a reference material, such as percent modern carbon (pMC), or as their per mil deviation ($\Delta^{14}C$). Correcting for isotopic fractionation effects is essential when accurate age determinations are performed using radiocarbon concentrations. Isotopic fractionation refers to changes in isotope ratios that occur through physical and chemical processes.

In this measurement method, the relationships among the various units and the procedures for correcting isotopic fractionation effects are described.

D.1 Per mil deviation from reference material ($\Delta^{14}C$)

Generally, the $^{14}C/^{12}C$ ratio is considered to experience twice the isotopic effect (isotopic fractionation) of the $^{13}C/^{12}C$ ratio. Based on this relationship, correction for isotopic fractionation of ^{14}C radioactivity concentrations requires the $\delta^{13}C$ value*155 of the reference material and sample.

The $\Delta^{14}C$ (‰) value is defined as the per mil deviation of the $^{14}C/^{12}C$ ratio in the sample (A_{SN}) relative to the $^{14}C/^{12}C$ ratio of the reference material (A_{abs}). It is defined by the following equation*156.

$$\Delta^{14}C = (A_{SN} / A_{abs} - 1) \times 1000$$

Here,

A_{SN} : ^{14}C decay rate per unit mass in the sample, or the $^{14}C/^{12}C$ ratio corrected for isotopic fractionation

A_{abs} : Value for the reference material corrected for isotopic fractionation and normalized to the value in the year 1950

Oxalic Acid I (SRM 4990) and Oxalic Acid II (SRM 4990C), distributed by the NIST, are widely used as radiocarbon reference materials.

The value of NIST oxalic acid I corrected for isotopic fractionation (A_{ON}) is defined as follows:

$$A_{ON} = 0.95 A_{OX} (1 - 19/1000)^2 / (1 + \delta^{13}C_{OX}/1000)^2$$

It can be approximated by the following expression:

$$A_{ON} = 0.95 A_{OX} [\ (1 - \{2(19 + \delta^{13}C_{OX})/1000\}]$$

A_{OX} : ^{14}C decay rate per unit mass, or the $^{14}C/^{12}C$ ratio, of NIST oxalic acid I (SRM 4990)

$\delta^{13}C_{OX}$: Deviation (‰) of the $^{13}C/^{12}C$ ratio of oxalic acid I (SRM 4990C) relative to the $^{13}C/^{12}C$ ratio of the standard reference material

The ^{14}C radioactive decay rate or $^{14}C/^{12}C$ ratio per unit mass of NIST oxalic acid I (SRM 4990)

*155 ^{13}C is expressed as the per mil deviation (‰) of the $^{13}C/^{12}C$ ratio of the sample relative to the $^{13}C/^{12}C$ ratio of the reference standard: $\delta^{13}C$ sample = ([$^{13}C/^{12}C$] sample/[$^{13}C/^{12}C$] reference standard − 1) × 1000

*156 Stuiver, M. and H. A. Polach: Discussion: Reporting of ^{14}C data. Radiocarbon, 19, 355-363 (1977).

was corrected to the value in 1950, normalized to $\delta^{13}C = -19‰$, and multiplied by 0.95[*157,*158].

Since NIST oxalic acid I (SRM 4990) has been depleted, when Oxalic Acid II (SRM 4990C) is used, the value is defined as follows[*159]:

$$A_{ON} = 0.7459 A_{NOX} (1 - 25/1000)^2 / (1 + \delta^{13}C_{NOX}/1000)^2$$

It can be approximated by the following expression:

$$A_{ON} = 0.7459 \ A_{NOX} \ [1 - \{2(25 + \delta^{13}C_{NOX})/1000\}]$$

A_{NOX} : ^{14}C decay rate per unit mass, or the $^{14}C/^{12}C$ ratio, of Oxalic Acid II (SRM 4990C)

$\delta^{13}C_{NOX}$: Deviation (‰) of the $^{13}C/^{12}C$ ratio of Oxalic Acid II (SRM 4990C) relative to the $^{13}C/^{12}C$ ratio of the reference standard (‰)

Because ^{14}C in reference materials also undergoes radioactive decay over time, correction for this decay is required. Thus, A_{ABS} is calculated using the following equation:

$$A_{ABS} = A_{ON} \exp(\lambda(y - 1950))$$

y : Year of measurement (AD)

λ : Decay constant = 1/8267 ($year^{-1}$)

A_{SN} can be expressed by the following approximate equation:

$$A_{SN} = A_{SA} [1 - \{2(25 + \delta^{13}C_{SA})/1000\}]$$

A_{SA} : ^{14}C decay rate per unit mass, or the $^{14}C/^{12}C$ ratio, in the sample

$\delta^{13}C_{SA}$: Deviation (‰) of the $^{13}C/^{12}C$ ratio in the sample relative to the $^{13}C/^{12}C$ ratio of the international reference standard

The value A_{SN} represents the ^{14}C radioactive decay rate of the sample, or $^{14}C/^{12}C$ ratio normalized to $\delta^{13}C = -25‰$[*160]. From the above, $\Delta^{14}C$ (‰) can be calculated. For more information on isotope fractionation effects and correction methods, refer to Kumamoto et al. (2015)[*161], Nakamura (1999)[*162], and Okouchi (2017)[*163].

If isotopic fractionation correction is not applied to the sample, the value is distinguished as follows:

$$\delta^{14}C(‰) = (A_{SA}/A_{abs} - 1) \times 1000$$

*157 Broecker, W. S. and Olson, E. A.: Lamont radiocarbon measurements VI, Radiocarbon, 1, 111–132 (1959)

*158 The factor 0.95 is used because NIST oxalic acid I (SRM 4990), produced in 1955, was slightly affected by atmospheric nuclear weapons tests and fossil fuel combustion. This correction converts the value to the ^{14}C abundance in trees grown around 1890, prior to significant anthropogenic influence

*159 Stuiver, M. : International agreements and the new oxalic acid standard. Radiocarbon, 25: 793-795 (1983)

*160 If the year of sample collection differs from the year of measurement, radioactive decay correction must also be applied to A_{SN}.

*161 熊本雄一郎、荒巻能史：海洋観測ガイドライン, Vol.3, Chap.9 (2015)

*162 中村俊夫：第 1 章：放射性炭素年代測定法, 長友恒人編、考古学のための年代測定学入門、古今書院, 1-36 (1999)

*163 大河内直彦：化合物レベル放射性炭素年代法, 地球化学, 51, 135-152 (2017)

D.2 Relative concentration with respect to standard reference material (percent modern carbon [pMC])

pMC is a unit that expresses the ^{14}C radioactivity concentration, where the carbon concentration in the year 1950 is defined as 100.

Since 100 pMC = 13.56 dpm/gC, the relationship between pMC and specific radioactivity of ^{14}C (Bq/gC) is expressed by the following equation*[164]:

$$C = 13.56/60 \times pMC/100$$
$$= pMC \times 0.00226$$

C: Specific radioactivity of ^{14}C (Bq/gC)

The relationship between pMC (%) and $\Delta^{14}C$ (‰) is expressed by the following equation:

$$pMC\ (\%) = ([\Delta^{14}C / 1000] + 1) \times 100$$

*164 Mook, W.G. and van der Plicht, J.:Reporting ^{14}C Activities and Concentrations, Radiocarbon, 41, 227-239(1999)

References

1) 岩倉哲男：原子力施設からの^{14}C, 日本原子力学会誌, Vol.35, No.10, 874 (1993)
2) United Nations Scientific Committee on the Effects of Atomic Radiation： UNSCEAR 2008 Report (2010)
3) Journal of Environmental Radioactivity, 166, 56-66 (2017)
4) Monitoring and Information Division, Nuclear Regulation Authority of Japan: About Normal Monitoring (Supplementary Reference to Nuclear Emergency Response Guidelines) (Revised on March 21, 2024), (Source: "Reference Materials"), (Revised on March 21, 2024)
5) 近藤美由紀：環境研究における自然トレーサーとしての放射性炭素(^{14}C)の利用, 国環研ニュース, 33 巻, 6 号 (2015)
6) 熊本雄一郎、荒巻能史：海洋観測ガイドライン, Vol.3, Chap.9 (2015).
7) IAEA：Management of Waste Containing Tritium and Carbon-14, Technical Reports Series, No.421 (2004)
8) World Data Centre: The World Data Centre for Greenhouse Gases
9) 石井雅男,吉川久幸,松枝秀和：電量滴定法による海水中の全炭酸濃度の高精度分析および大気中の二酸化炭素と海水中の全炭酸の放射性炭素同位体比の測定,気象研究所技術報告第41 号, 1-71 (2000).
10) 亀尾 裕,島田 亜佐子, 石森 健一郎, 原賀 智子,片山 淳, 星 亜紀子,中島 幹雄：研究施設等廃棄物に含まれる放射性核種の簡易・迅速分析法(分析指針), JAEA Technology, 2009-051 (2009)
11) 関 晃太郎,佐々木 誉幸,秋元 友寿,徳永 貴仁,田中 究,原賀 智子,上野 隆,石森 健一郎, 星 亜紀子,亀尾 裕：福島第一原子力発電所の廃止措置に向けた瓦礫・植物などの放射性核種分析手法に関する検討, JAEA Technology, 2016-013 (2016)
12) JIS Z 8404-1：測定の不確かさ−第 1 部, JIS Z 8404-1:2018 (2018)
13) J.A Cooper: Factors determining the ultimate detection sensitivity of Ge (Li) gamma-ray spectrometers, Nuclear Instruments and Methods, 82, 273-277 (1970)
14) H.Kaiser : Zum Problem der Nachweisgrenze, Analytisehe Chemie, 209, 1-18 (1965)
15) 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 & Applied Chemistry, 45, 105-123 (1976)
16) 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)
17) L.M.Cavallo and W.B.Mann: International reference material for contemporary carbon-14 oxalic acid RM-49, National Bureau of Standards Report of Investigation (1980)
18) IAEA：Reference sheet for quality control materials (2014)
19) Rozanski, K.: Consultants' group meeting on ^{14}C reference materials for radiocarbon laboratories. 1991, Internal Report, IAEA, Vienna (1991).

20) ENSDF (Evaluated Nuclear Structure Data File) (as of October 2023)
21) 松崎浩之: 加速器質量分析の原理, Journal of the Vacuum Society of Japan, 50(7),467-474 (2007)
22) Saito-Kokubu, Y., Matsubara, A., Fujita, N., Kuwabara, J., & Kinoshita, N.：JAEA-AMS-TONO 及び JAEA-AMS-MUTSU 間での炭素同位体標準試料測定の比較試験結果. ,JAEA Technology (2022)
23) 小田寛貴, 中村俊夫, & 古川路明：名古屋大学タンデトロン加速器質量分析計による古文書資料の ^{14}C 年代測定, 名古屋大学加速器質量分析計業績報告書, IX, 324-334(1998)
24) 中村俊夫：加速器質量分析 (AMS) 法による^{14}C 年代測定の高精度化及び正確度向上の検討, 第四紀研究, 34(3), 171-183 (1995).
25) 北川浩之, 中村俊夫, & 福沢仁之：水月湖湖底・年縞堆積物の AMS-^{14}C 年代, 名古屋大学加速器質量分析計業績報告書, VI, 27-42 (1995).
26) 松崎浩之：東大 MALT における加速器ビーム分析システムの現状, 応用物理学会学術講演会講演予稿集 第 67 回応用物理学会春季学術講演会, 591 (2020)
27) 亀尾裕、島田亜佐子、石森健一郎、原賀智子、片山淳、星亜紀子、中島幹雄：研究施設等廃棄物に含まれる放射性核種の簡易・迅速分析法(分析指針), JAEA-Technology, 2009-51 (2009)
28) 上野有美、小嵐淳、岩井保則、佐藤淳也、高橋照彦、澤畠勝紀、関田勉、小林誠、角田昌彦、菊地正光：RI 施設における排気中 ^{14}C モニタリング：捕集及び酸化方法の比較評価,Jpn. J. Health Phys., 49(1), 39-44 (2014)
29) G. Wakabayashi, H. Ohura, T. Okai, M. Matoba, H. Kakiuchi, N. Momoshima, H. Kawamura, Stability and reproducibility of gel-suspension samples for the liquid scintillation counting of ^{14}C using N-lauroyl-L-glutamic-α,γ- dibutylamide, Radioanalytical and Nuclear Chemistry, Vol. 240, No. 3, 929-930 (1999)
30) K. Pfeiffer, D. Rank and M. Tschurlovits: A Method for Counting ^{14}C as CaC03 in a Liquid Scintillator with Improved Precision, Applied Radiation and Isotopes, 32, 665-667 (1981)
31) (財)日本分析センター：環境試料中炭素14 迅速分析法, 16 環境委報告001 (2005)
32) G. Wakabayashi, H. Ohura, T. Okai, M. Matoba, A. Nohtomi, H. Kakiuchi, N. Momoshima, H. Kawamura: Simple measurement of ^{14}C in the environment using a gel suspension method, Radioanalytical and Nuclear Chemistry, Vol 239, No.3, 639-642 (1999)
33) Broecker, W. S. and Olson, E. A.: Lamont radiocarbon measurements VI, Radiocarbon, 1, 111–132 (1959)
34) Stuiver, M.: International agreements and the new oxalic acid standard. Radiocarbon, 25, 793-795 (1983)
35) 中村俊夫：第1 章：放射性炭素年代測定法, 長友恒人編、考古学のための年代測定学入門、古今書院, 1-36 (1999)
36) 大河内直彦：化合物レベル放射性炭素年代法, 地球化学, 51, 135-152 (2017)
37) Mook, W.G. and van der Plicht, J.:Reporting ^{14}C Activities and Concentrations, Radiocarbon, 41, 227-239(1999)

Revision History

Established in November 1993

Revised June 2025