The Series of Environmental Radioactivity Measuring Methods

AN-I129
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# Iodine-129 Analysis

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Radiation Monitoring Division
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# Introduction

Iodine-129 ($^{129}$I) has a long half-life of 15.7 million years. Due to its chemical properties, it persists in the environment for extended periods. Furthermore, it is known to circulate in the atmosphere, terrestrial environments, and marine environments through various environmental samples. Hence, it is regarded as one of the important radionuclides in environmental impact assessments. Natural sources of $^{129}$I include cosmic ray reactions. Meanwhile, anthropogenic sources include nuclear tests, nuclear fuel reprocessing plants, and nuclear facility accidents. It is important to understand the levels of radioactivity in the environment to assess their impacts.

As per "Routine Monitoring (Supplementary Material for Guidelines for Emergency Preparedness and Response for Nuclear Incidents/Disasters)," the primary radionuclides contributing to radiation exposure to surrounding residents and others are identified for routine monitoring in the vicinity of reprocessing plants. The contribution ratio of $^{129}$I to the total facility-induced radiation dose and the measurement mean are not determined in routine monitoring measurements. Monitoring in the vicinity of reprocessing plant requires understanding long-term accumulation patterns and fluctuation trends of radionuclides while considering the operational status of facilities. To ensure the thorough and systematic implementation of detailed environmental radiation monitoring measures outside the premises of Fukushima Daiichi Nuclear Power Plant operated by Tokyo Electric Power Company, Incorporated (TEPCO), in relation to the TEPCO Fukushima Daiichi Nuclear Power Station Accident (hereinafter referred to as the "1F Accident"), the government established a Monitoring Coordination Council under the Nuclear Emergency Response Headquarters and formulated a Comprehensive Radiation Monitoring Plan. This monitoring plan requires the identification of long-term trends during the monitoring of seawater and marine organisms.

The analysis and measurement of $^{129}$I are conducted using analytical methods tailored to various research objectives. $^{129}$I was considered to be one of the radionuclides released during the 1F accident. Hence, environmental samples, including airborne particulate matter, soil, marine sediments, and seawater were analyzed for verifying the presence of this radionuclide. Numerous associated reports and research papers have been published, including those focusing on employing $^{129}$I to estimate the concentration of the short half-life radionuclide $^{131}$I[*i].

Two methods for $^{129}$I analysis are presented in the The Series of Environmental Radioactivity Measuring Methods No. 26 "Iodine-129 Analysis" (1996), which targets low-level environmental samples, and The Series of Environmental Radioactivity Measuring Methods No. 32 "Rapid Analysis Method for Iodine-129 in Environmental Samples" (2004), which emphasizes rapid analysis. For routine monitoring, The Series of Environmental Radioactivity Measuring Methods No. 26 should be used. Meanwhile, for emergency monitoring, The Series of Environmental Radioactivity Measuring Methods No. 32 should be used.

Under these circumstances, the revised The Series of Environmental Radioactivity Measuring Methods Series No. 26 “Iodine-129 Analysis Method” adopts the radiochemical analysis methods implemented by local governments and operators for environmental radiation monitoring around reprocessing plants as well as the triple quadrupole inductively coupled plasma mass spectrometry method (hereinafter referred to as the “triple quadrupole ICP–MS method”)[*ii] and accelerator mass spectrometry used by research institutions to analyze environmental samples for various survey and research purposes. Regarding neutron activation analysis, it was decided to remove this method because it is not used by any analytical institutions, primarily due to factors such as the high cost of managing radiation exposure to analysts. To read the neutron activation analysis methods omitted in this revision please refer to the archived version of the first edition of this measurement method.

The following text outlines the three analytical techniques adopted in this measurement method: radiochemical analysis, triple quadrupole ICP–MS, and accelerator mass spectrometry.

Radiochemical Analysis:

This technique involves preparing the measurement sample using analytical procedures appropriate for the sample, followed by measuring the β-rays or γ-rays emitted by $^{129}$I. The β-rays and γ-rays have energies of 189.3 and 39.578 keV, respectively, both of which are very low (see “Common Appendix A $^{129}$I Nuclear Data and Decay Chart”). Therefore, chemical separation is required to measure $^{129}$I in typical environmental samples, and measurement is performed using low-energy photon spectrometers, n-type germanium semiconductor detectors, or low-background gas flow counters. For each type of sample, iodine is purified via solvent extraction after performing pretreatment procedures such as combustion or ion exchange. The generated product is a palladium(II) iodide precipitate, which is used as the measurement sample. Further, a counting efficiency curve is generated using a standard solution with a known concentration of $^{129}$I, and $^{129}$I in the measured sample is then quantified. This analytical method is widely implemented using commonly available equipment and instruments.

Triple Quadrupole ICP–MS Analysis:

This technique involves preparing a measurement solution through analytical procedures tailored to the sample, followed by measuring the target mass number. For triple quadrupole ICP–MS analysis, detectable levels were established by referring to environmental samples (seawater and seaweed) and detection limits specified in the Comprehensive Radiation Monitoring Plan. The triple quadrupole ICP–MS device features a structure where a collision reaction cell is sandwiched between two quadrupoles.

ICP–MS suffers from spectral interference caused by ions with the same mass-to-charge ratio ($m/z$) as the target ion. In $^{129}$I analysis, $^{129}$Xe present as an impurity in argon gas, oxides of $^{97}$Mo and $^{113}$Cd, and the hydrogen compound of stable iodine $^{127}$I are the primary causes of spectral interference. This interference must be carefully considered when performing analysis and measurements. When formulating the measurement method, we referred to the General Specifications for Inductively Coupled Plasma Mass Spectrometry (Japanese Industrial Standard (JIS) K 0133:2022) and paid attention to the terminology used and the names of reagents.

Furthermore, the validity of the analytical method was confirmed by conducting comparative analyses with other analytical institutions. This analytical technique has a lower detection limit than radiochemical analysis and has become increasingly widespread in recent years. However, the equipment used is more expensive.

Accelerator Mass Spectrometry:

In this technique, the target sample is prepared through specific methods tailored to the sample. Then, $^{127}I$ and $^{129}I$ are separated using an accelerator and analyzed. In particular, after pretreatments, such as thermal hydrolysis, pertaining to each sample type, the samples are purified via solvent extraction and silver iodide precipitation. Generated silver iodide is mixed with niobium metal powder and pressed into a "target piece" suitable for loading into the ion source of the accelerator. This represents the measurement sample in accelerator mass spectrometry and is generally called the "target." Since the target piece acts as the cathode in the ion source, it is also referred to as the "cathode." This analytical method is currently the most sensitive method for quantifying $^{129}I$. Notably, equipment for accelerator mass spectrometry (hereinafter referred to as "AMS") are extremely large and expensive and therefore not widely available. In Japan, the number of analytical institutions capable of performing such measurements is limited[*iii].

This measurement method series outlines common techniques used in environmental radiation monitoring. However, it does not exclude new technologies, including those involving ever-advancing analytical techniques. It is necessary to select analytical methods based on the intended purpose and required analytical precision.

The sample sizes and detection limits for each analytical method are presented in Tables 1.1–1.3.

Table 1.1 Sample size and detectable level of radiochemical analysis

| Sample name | Analytical sample amount | Detectable level[*iv] | Unit |
|---|---|---|---|
| Airborne particulate matter | 1,000 $m^3$ | $5 \times 10^{-4}$ | $Bq/m^3$ |
| Seawater | 5 L | $1 \times 10^{-1}$ | Bq/L |
| Inland waters | 5 L | $1 \times 10^{-1}$ | Bq/L |
| Soil | 100 g (dry) | $5 \times 10^{0}$ | Bq/kg dry soil |
| Vegetables | 30 g (dried) | $2 \times 10^{0}$ | Bq/kg raw |
| Seaweed | 30 g (dried) | $4 \times 10^{0}$ | Bq/kg raw |
| Milk | 5 L | $1 \times 10^{-1}$ | Bq/L |
| Polished rice | 50 g | $1 \times 10^{1}$ | Bq/kg |

Table 1.2 Sample quantity and detectable level for triple quadrupole ICP–MS analysis

| Sample name[*v] | Analytical sample amount | Detectable level[*iv] | Unit |
|---|---|---|---|
| Airborne particulate matter | 300 $m^3$ | $9 \times 10^{-7}$ | $Bq/m^3$ |
| Seawater | 1 mL | $7 \times 10^{-3}$ | Bq/L |
| Inland water | 1 mL | $7 \times 10^{-3}$ | Bq/L |
| Soil | 1 g (dry) | $3 \times 10^{-1}$ | Bq/kg dry soil |
| Vegetables | 2 g (dried)<br>(Equivalent to 20 g raw) | $1 \times 10^{-2}$ | Bq/kg raw |
| Seaweed | 0.6 g (dried)<br>(Equivalent to 3 g raw) | $9 \times 10^{-2}$ | Bq/kg raw |
| Milk | 20 mL | $2 \times 10^{-2}$ | Bq/L |

Appendix 1.3 Sample quantity for analysis and detectable levels of accelerator mass spectrometry

| Sample name | Analytical sample amount | Detectable level[*iv] | Unit |
|---|---|---|---|
| Airborne particulate matter | 300 $m^3$ | $3 \times 10^{-15}$ | $Bq/m^3$ |
| Seawater | 1 L | $8 \times 10^{-11}$ | Bq/L |
| Inland waters | 1 L | $2 \times 10^{-11}$ | Bq/L |
| Soil sample | 1 g (dry) | $2 \times 10^{-9}$ | Bq/kg dry soil |
| Vegetables | 2 g (dried)<br>(Equivalent to 20 g raw) | $2 \times 10^{-10}$ | Bq/kg raw |
| Seaweed | 0.5 g (dried)<br>(Equivalent to 2.5 g raw) | $2 \times 10^{-6}$ | Bq/kg raw |
| Milk | 20 mL | $3 \times 10^{-10}$ | Bq/L |

[*i] The following reports describe cases where $^{131}I$ was estimated using $^{129}I$.
文部科学省 原子力災害対策支援本部、農林水産省 農林水産技術会議事： 東京電力株式会社福島第一原子力発電所の事故に伴い放出された放射性物質の分布状況等に関する調査研究結果 (2012)
(https://radioactivity.nra.go.jp/ja/list/338/list-1.html)
Note that the content of the above report is also cited in the UNSCEAR 2020/2021 Report issued by the United Nations in 2022.

[*ii] The International Union of Pure and Applied Chemistry (IUPAC) defines a triple quadrupole mass spectrometer as "a tandem mass spectrometer comprising two transmission quadrupole mass spectrometers in series, with a (nonselecting) RF-only quadrupole (or other multipole) between them acting as a collision cell." The essence of this analytical method lies not in the number of quadrupoles but in the mass analysis capability realized by the quadrupoles placed before and after the cell. Different manufacturers have differing names to these instruments. Examples (in Japan) include Agilent Technologies Inc.'s "Triple Quadrupole Inductively Coupled Plasma Mass Spectrometer," Thermo Fisher Scientific's

"Triple Quadrupole ICP Mass Spectrometry," and PerkinElmer Japan's "Multi Quadrupole ICP Mass Spectrometer." The measurement method uses the designation "Triple Quadrupole Inductively Coupled Plasma Mass Spectrometry/Spectrometer" (Triple Quadrupole ICP–MS).

[*iii] Accelerators capable of $^{129}I$ AMS analysis include those manufactured by National Electrostatics Corporation (NEC; USA), High Voltage Engineering Europa (HVEE; Netherlands), and Ionplus (Switzerland). In Japan, accelerators from NEC and HVEE are available. In 2023, facilities in Japan capable of performing $^{129}I$ AMS analysis included the Japan Atomic Energy Agency's Aomori Research and Development Center, the same agency's Tono Geoscience Center, the University of Tokyo's Micro Analysis Laboratory,Tandem accelerator, the University of Tsukuba's Center for Research in Radiation,Isotopes, and Earth System Sciences, and the National Institute for Environmental Studies.

[*iv] Detectable levels were calculated under the following conditions.

1. Radiochemical Analysis:

   ① Measurements were performed using a low-energy photon spectrometer. Conditions: Counting efficiency: 0.5%, measurement time: 20 hours, and recovery rate: 60%.

   ② Measurements were performed using a low-background gas flow counter. Conditions: Counting efficiency: 4%, measurement time: 100 minutes, and recovery rate: 60%.

   In radiochemical analysis, the detection limit was set as three times the counting error associated with the net counting rate.

2. Triple Quadrupole ICP–MS Analysis:

   Measurements were performed using a triple quadrupole ICP–MS device (coaxial nebulizer)

   Conditions: Detection limit: 0.02 ng/L, recovery rate: 100%, dilution factor: 50-fold for seawater and 100-fold for seaweed. Values for samples other than seawater and seaweed are hypothetical.

   For the triple quadrupole ICP–MS analysis, the detection limit was defined as three times the standard deviation of the background count value measured over 10 consecutive 10-second intervals.

3. Accelerator Mass Spectrometry:

   The atomic ratio ($^{129}I/^{127}I$) in the AMS measurement sample must not fall below the atomic ratio of the added iodine carrier. Under this condition, the AMS determination limit is an atomic ratio of $2 \times 10^{-14}$, atomic ratio of the iodine carrier is $2 \times 10^{-13}$, amount of iodine carrier added is 10 mg for solid samples and 2 mg for liquid samples.

   The concentration of $^{127}I$ in the sample was calculated using the following values.

   Airborne particulate matter : $2 \times 10^{-6}$ mg/m$^3$

   Seawater : $6 \times 10^{-2}$ mg/L

   Inland water : $1 \times 10^{-2}$ mg/L

   Soil sample : $1 \times 10^{0}$ mg/kg dry soil

   Vegetables : $1 \times 10^{-1}$ mg/kg raw

   Seaweed : $1 \times 10^{3}$ mg/kg raw

   Milk : $2 \times 10^{-1}$ mg/L

4. The weight ratio of dried foods to raw vegetable samples was set at 10%.

5. The weight ratio of dried foods to raw seaweed samples was set at 20%.

[*v] Although not described in the main text, analyzable samples are also listed.

# I. Radiochemical Analysis

# Chapter 1 Airborne Particulate Matter

For analysis, airborne particulate matter are separated and purified using either the activated-carbon adsorption method, wherein an activated-carbon filter paper or activated-carbon cartridges containing absorbed particulates are incinerated to adsorb iodine onto activated carbon, or the alkali-solution absorption method, wherein particulates are absorbed into an alkali solution.

Note that the amount of stable iodine (hereinafter referred to as "$^{127}$I") in airborne particulates[*1] is small. Since 20 mg of an iodine carrier is added before analysis, the amount of iodine in the sample has little effect on the recovery rate. Therefore, the determination of $^{127}$I in the sample is not performed.

## 1.1 Preparation of Reagents

The following text describes the preparation method for reagents used in the radiochemical analysis of airborne particulate matter. Reagents should be of the JIS Special Grade. Unless otherwise specified, commercially available products should be used as is. The term "pure water" used here refers to water purified by ion exchange or similar processes.

(1) Base:

1) Sodium hydroxide solution (24 w/v%): Dissolve 24 g of sodium hydroxide[*2,*3] in 100 mL of pure water.
2) Potassium hydroxide solution (5 w/v%): Dissolve 5 g of potassium hydroxide[*2,*3] in 100 mL of pure water.

(2) Other solutions:

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*3,*4] in 100 mL of pure water.
2) Potassium nitrite solution (10 w/v%): Dissolve 10 g of potassium nitrite[*3,*4] in 100 mL of pure water.
3) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of pure water.
4) Potassium sulfite solution (10 w/v%): Dissolve 10 g of potassium sulfite in 100 mL of pure water.

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[*1] The amount of $^{127}$I in airborne particulate matter varies depending on the collection site and weather conditions. The maximum amount contained in 1,000 m$^3$ of air is approximately 0.002 mg.

[*2] Substances subject to labeling requirements under the Industrial Safety and Health Act (those posing potential hazards or health risks to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*3] 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." Further, necessary measures must be taken to prevent theft, loss, leakage, or other incidents.

[*4] Classified as Class 1 Hazardous Materials (Oxidizing Solids) under the Fire Service Act. Avoid contact with strong acids; store away from combustible materials; and prevent heating, impact, or friction.

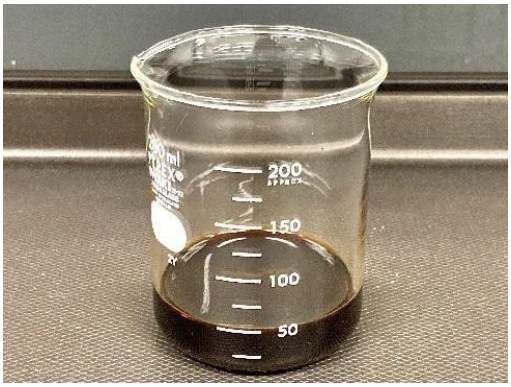
5) Palladium chloride solution (10 mgPd/mL): Weigh 1.7 g of palladium chloride, add 50 mL of pure water and 5 mL of 36% hydrochloric acid[*2,*3,*5] to it, and heat the resulting solution. Next, allow the solution to cool and then filter it (using the No. 5C filter paper). Subsequently, add pure water to the filtrate so that the final volume is 100 mL. (Refer to Figure I.1.1 while performing the operation.)
6) Iodine carrier solution (20 mgI/mL): Dry approximately 14 g of sodium iodide[*2] at 110°C for 3 hours; then, cool it for 1 hour in a desiccator. Weigh 11.812 g and dissolve in 50 mL of pure water. Then, transfer the resulting solution in a brown 500 mL volumetric flask containing 0.2 mL of the sodium hydroxide solution (24 w/v%) and 1 mL of the sodium sulfite solution (10 w/v%). Then, add pure water up to the mark on the volumetric flask. Finally, store in a cool, dark place.



(1) Weigh palladium chloride.




(2) Add pure water to palladium chloride.




(3) Add hydrochloric acid and heat.



(4) Allow the solution to cool and then filter it.

[*5] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, are required.



(5) Obtain the residue after filtration.




(6) Add pure water to the filtrate so that the final volume is 100 mL.

Figure I.1.1 Preparation of the palladium chloride solution

## 1.2 Combustion–Activated Carbon Adsorption Method

### 1.2.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Three-chamber tubular electric furnace (Figure I.1.2)
2) Dryer
3) Balance (weighing range of 0–200 g; readability of ≤0.1 mg)

(2) Instruments

1) Quartz tube (Figure I.1.3)
2) Silicone stopper
3) Quartz wool
4) Beaker (100 mL)
5) Watch glass (for 100 mL beakers)
6) Erlenmeyer flask (50 mL)
7) Air cooling tube (approximately 30 cm in length; to be attached to a 50 mL Erlenmeyer flask)
8) Separatory funnel (100 mL)
9) 1 L pressure bottle
10) Separable filter holder for 20 mm diameter and 42 mm diameter filters
11) Aspirator
12) Glass funnel (for a 90 mm diameter filter paper)
13) Filter paper
    - Glass-fiber filter paper (47 mm diameter)
    - Separatory filter paper (90 mm diameter)
    - No. 5C filter paper (24 mm diameter)
14) Mounting apparatus
    - Mounting disk (Figure I.1.4)

・Polyethylene terephthalate (PET) film[*6] (Figure I.1.4; ≤0.8 mg/m$^2$)
・Ring (Figure I.1.4; Outer diameter: 24 mm; Inner diameter: 21.8–21.9 mm)
・Stainless steel sample dish (25 mm diameter)
・Holding device (Figure I.1.5)

15) Micropipette (1 mL and 5 mL)
16) Pipette tips (1 mL and 5 mL)
17) Hand burner (for city gas or propane gas)
18) Desiccator
19) Hot plate

(3) Reagents

1) Nitric acid[*7,*8,*9] (mass fraction: 60%–61% (approximately 13 mol/L); density: 1.38 g/mL)
2) Sodium hydroxide solution (24 w/v%)
3) Sodium nitrite solution (10 w/v%)
4) Sodium sulfite solution (10 w/v%)
5) Palladium chloride solution (10 mgPd/mL)
6) Iodine carrier solution (20 mgI/mL)
7) Xylene[*8,*9,*10,*11]
8) Pure water (purified by ion exchange or similar processes)
9) Activated carbon
10) Copper oxide[*8] (needle-shaped)
11) Gases
・Oxygen gas (purity ≥ 99.999%)
・Nitrogen gas (purity ≥ 99.99%)
・City gas or propane gas

## 1.2.2 Analytical Operations

(1) Pretreatment

1) Fill the inner tube of the quartz tube (Figure I.1.2) as densely as possible with the

[*6] Before use, verify the degree of shielding using standard samples or similar materials and confirm that it does not affect the radioactivity measurement results.
[*7] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, are required.
[*8] Substances subject to labeling requirements under the Industrial Safety and Health Act (those posing potential hazards or health risks to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.
[*9] 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, or other incidents.
[*10] Class II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, are mandatory.
[*11] Guidelines for Prevention of Health Hazards from Chemical Substances Designated by the Ministry of Health, Labor and Welfare in accordance with Article 28, Paragraph 3 of the Industrial Safety and Health Act: Measures must be implemented to reduce exposure to target substances.

activated-carbon filter paper or activated-carbon cartridges that have absorbed approximately 1,000 $m^3$ of air[*12]. When doing so, prepack the narrower end of the inner tube with quartz wool.

2) Add 1 mL of the iodine carrier solution (20 mgI/mL) to the filled sample and seal the end with quartz wool.

(2) Combustion of samples

1) Pack quartz wool into the narrow section of the outer tube, add 3 g of activated carbon, and seal the end with quartz wool. (Refer to Figures I.1.2 and I.1.3 while performing the operation.)
2) Pack the section located at Electric Furnace (B) of the outer casing with quartz wool[*13] wrapped around needle-shaped copper oxide acting as a catalyst.
3) Attach the outer tube to the combustion device, and install the inner tube inside the outer tube.
4) Set the temperature of the activated-carbon heating furnace (C) to 150°C.
5) Supply nitrogen gas to the inner tube at a flow rate of 100 mL/min. Supply oxygen gas to the outer tube at a flow rate of 200 mL/min.
6) Set the temperature of Electric Furnace (B) to 1000°C.
7) Position Electric Furnace (A) at the right edge of the sample, and set the temperature to 240°C.
8) While monitoring the tar generation and carbonization conditions, gradually move Electric Furnace (A) toward Electric Furnace (B). Maintain a constant flow rate of oxygen and nitrogen gases[*14].
9) After moving Electric Furnace (A) until it touches Electric Furnace (B), raise the temperature of Electric Furnace (A) to 280°C and operate it for ~1 hour.
10) If combustion is stable, raise the temperature of Electric Furnace (A) to 350°C to drive combustible components out of the sample and achieve complete combustion in Electric Furnace (B). Maintain this state for 2–3 hours. The time required to reach 350°C varies depending on the sample condition. Increase the temperature while monitoring combustion, and avoid pressure buildup inside the quartz tube.
11) After the combustible components have finished burning, move Electric Furnace (A) to the far right end of the sample.
12) Set the temperature of Electric Furnace (A) to 400°C, supply oxygen gas to the inner tube at a rate of 50 mL/min, and combust the carbonized sample. Additionally, adjust the nitrogen flow rate as appropriate.
13) Gradually move Electric Furnace (A) toward Electric Furnace (B) and reduce the nitrogen-gas flow rate in the inner tube.

[*12] Activated carbon is highly combustible. Because sudden combustion reactions are more likely, it should be packed as tightly as possible without gaps.
[*13] To increase the combustion efficiency of the sample, quartz wool containing needle-shaped copper oxide is packed as a catalyst.
[*14] When a rapid combustion reaction occurs, the flow meter may exceed its scale.

14) While monitoring the combustion state, raise the temperature of Electric Furnace (A) to 600°C. If combustion becomes very intense, lower the temperature.
15) Set the oxygen gas flow rate in the inner tube to 100 mL/min and continue combustion.
16) After Electric Furnace (A) reaches Electric Furnace (B), return Electric Furnace (A) to the center of the sample. Raise the temperature to 1000°C and completely combust the sample. When tar accumulates at the outlet of the inner pipe, combustion may temporarily intensify; hence, monitor the combustion while raising the temperature.
17) Set the temperature of Electric Furnace (B) to 500°C and turn off the switch for Electric Furnace (A).
18) After sample combustion is complete, pack the narrow section of the trap tube with quartz wool, insert 0.5 g of activated carbon, and seal the end with quartz wool. Connect the trap pipe to the ball joint at the left end of the outer pipe using a clamp. Shift the outer pipe to the right so that the trap pipe aligns with Electric Furnace (C) and the right end of Activated Carbon (D) aligns with the left end of Electric Furnace (B). Pass oxygen gas at a flow rate of 50 mL/min through the outer and inner tubes.
19) Adjust the flow rate of oxygen gas in the inner tube while monitoring the ignition and combustion state of Activated Carbon (D) and the pressure inside the quartz tube.
20) After the activated carbon has finished burning, heat the joint area with a hand burner to burn off any remaining tar residue. Gradually move Electric Furnace (B) to the left to completely combust the activated carbon.

(3) Chemical separation of iodine after combustion

1) Transfer activated carbon adsorbing iodine in a 50 mL Erlenmeyer flask and add 20 mL of the sodium hydroxide solution (24 w/v%). Attach an air-cooled condenser (approximately 30 cm long) to the Erlenmeyer flask and gently heat it on a hot plate for ~1 hour to extract iodine.
2) After cooling, remove the air-cooling tube, perform suction filtration (using a 47 mm diameter glass-fiber filter, a separable filter holder, and a pressure-resistant bottle), and wash activated carbon with pure water. Combine the filtrate and a washing solution. Then, transfer the mixture in a 100 mL separatory funnel containing 20 mL of xylene.
3) While stirring (by rotating the separatory funnel), add approximately 8 mL of nitric acid to adjust the pH to 1[*15].
4) Gradually add 5 mL of the sodium nitrite solution[*16] (10 w/v%). Shake the separatory funnel vigorously for 2 minutes while periodically releasing gases[*17].
5) After allowing it to settle, transfer the aqueous phase to a new 100 mL separatory funnel containing 20 mL of xylene[*18]. Transfer the organic phase in a separate 100 mL separatory

[*15] Verify using a pH test paper.
[*16] Oxidize $I^-$ to $I_2$.
[*17] The organic phase changes from colorless to pink.
[*18] In addition to xylene, benzene and toluene can be used. However, care must be taken to ensure safety during their use. Iodine recovery rates obtained when using different organic solvents are 91% (xylene), 99% (benzene), and 84% (toluene).

funnel while filtering (using a 90 mm diameter separatory filter paper and glass funnel).

6) Shake the separatory funnel containing the aqueous phase mentioned in Step 5 vigorously for 2 minutes. After allowing it to settle, discard the aqueous phase. Transfer the organic phase in the separatory funnel containing the organic phase mentioned in Step 5 while filtering (using a 90 mm diameter separatory funnel paper and glass funnel).
7) Add 20 mL of pure water and shake vigorously for 2 minutes to wash the organic phase. Then, discard the aqueous phase.
8) Add 20 mL of pure water and 0.5 mL of the sodium sulfite solution[*19] (10 w/v%) to a separatory funnel. Shake vigorously for 2 minutes while occasionally releasing gases[*20].
9) Transfer the aqueous phase to a 100 mL beaker. Leave the organic phase in the separatory funnel and add 20 mL of pure water.
10) Shake the separatory funnel vigorously for 2 minutes while occasionally releasing gases.
11) Adjust the liquid phase to the 100 mL beaker mentioned in Step 9. Discard the organic phase.
12) Cover the beaker with a watch glass and heat it on a hot plate until xylene evaporates completely. After cooling, add 3 mL of the palladium chloride solution (10 mgPd/mL) and heat to boiling. (Refer to Figure I.1.6 while performing the operation.)
13) After cooling, suction-filter the precipitate (using a filter paper of known weight (No. 5C; 24 mm diameter), a separable filter holder, and a pressure bottle). Discard the filtrate. Dry the precipitate together with the filter paper in a drying oven at 80°C for 1 hour. Then, allow it to cool for 30 minutes in a desiccator. Measure the weight of the precipitate.
14) Place the precipitate with the filter paper onto the mounting disk, cover with a PET film, and secure with a ring. Trim any film protruding from the ring, and then transfer it to the sample dish. Subsequently, use it as the measurement sample. (Refer to Figures I.1.5 and I.1.7 while performing the operation.)

[*19] Reduce $I_2$ to $I^-$.
[*20] The organic phase changes from pink to colorless.

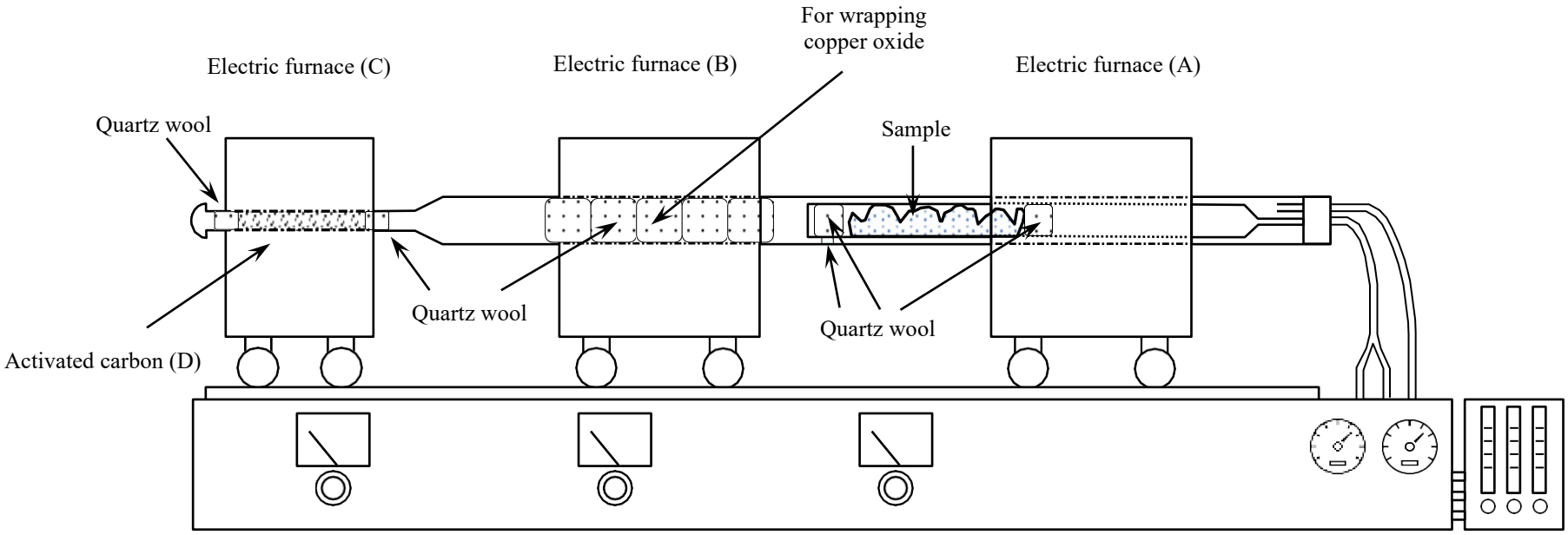
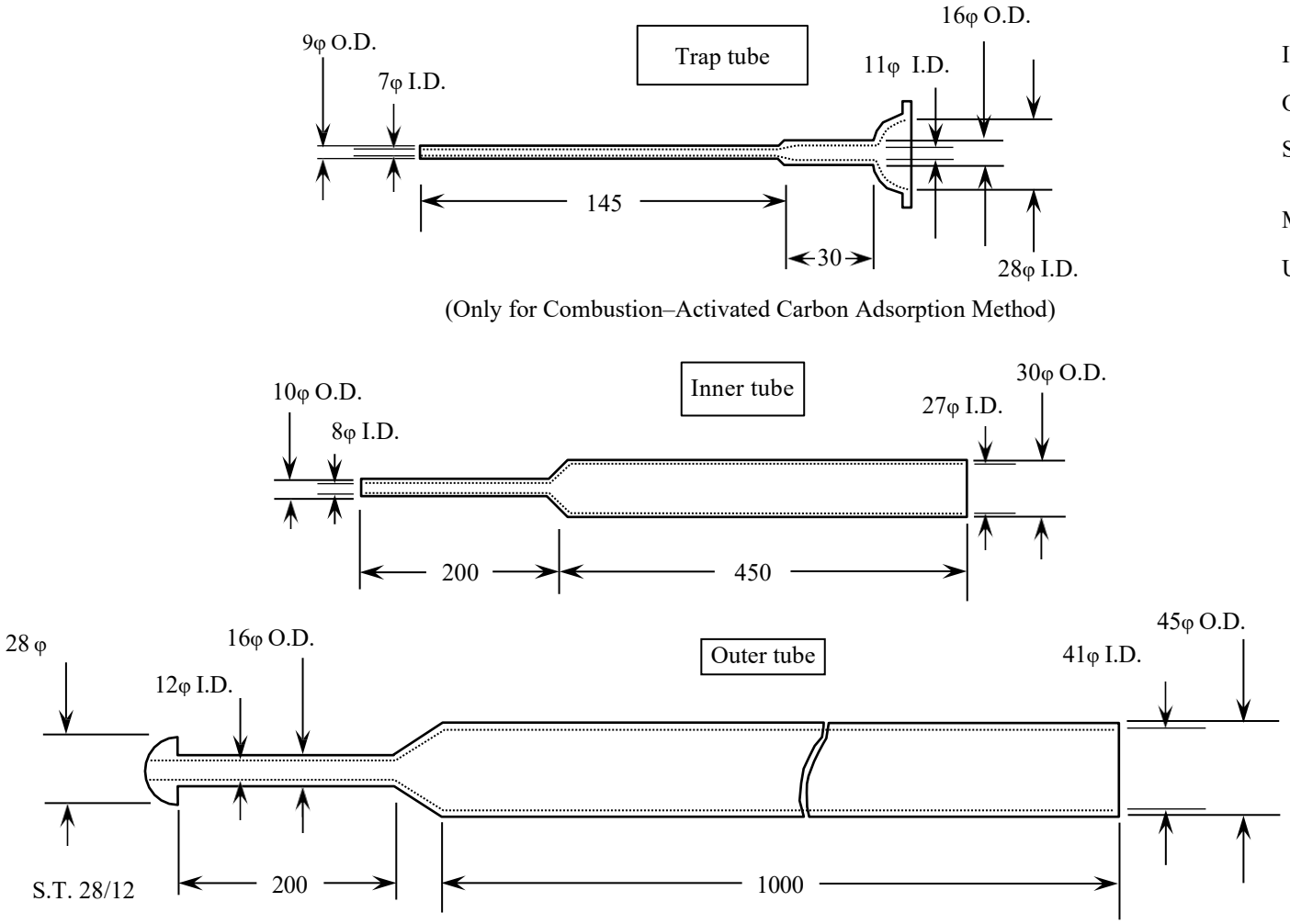



Figure I.1.2 Three-chamber tubular electric furnace




I.D.: Inner diameter;

O.D.: Outer diameter

S.T.: Standard taper

Material: Transparent quartz

Unit: mm

(Only for Combustion–Activated Carbon Adsorption Method)

Figure I.1.3 Quartz tube

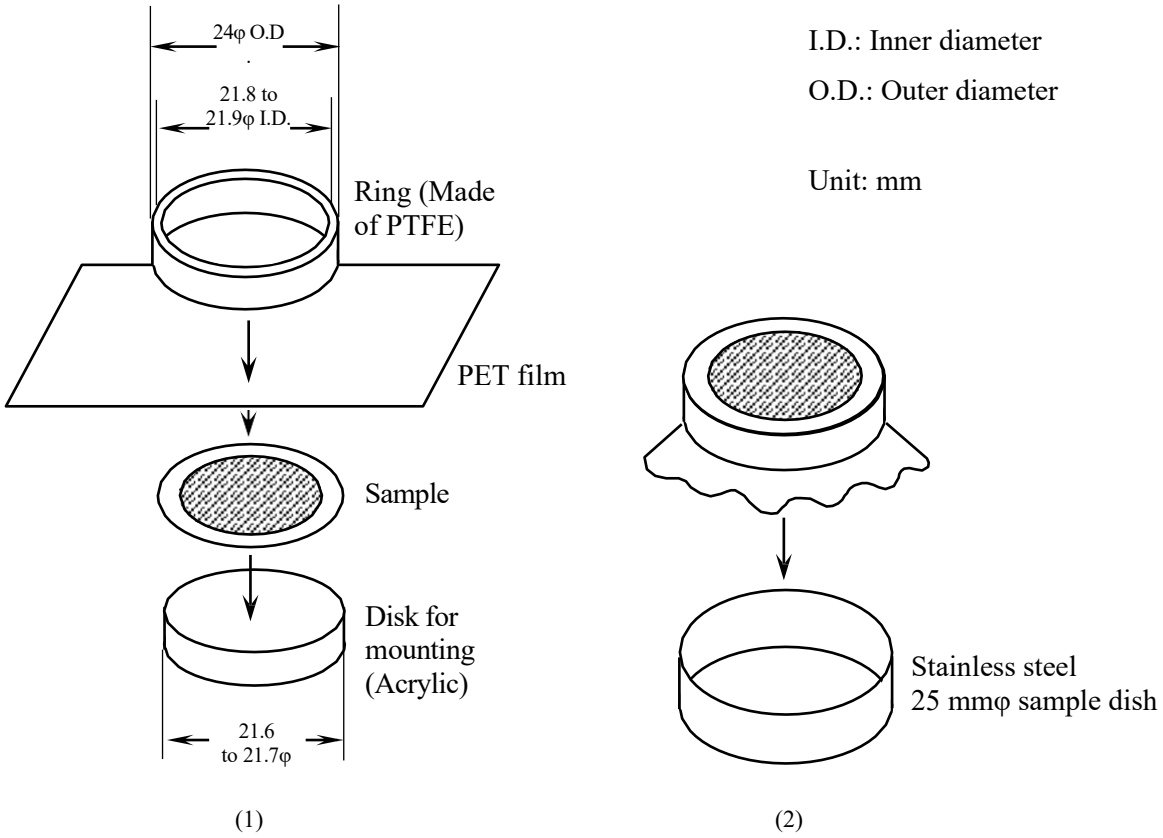
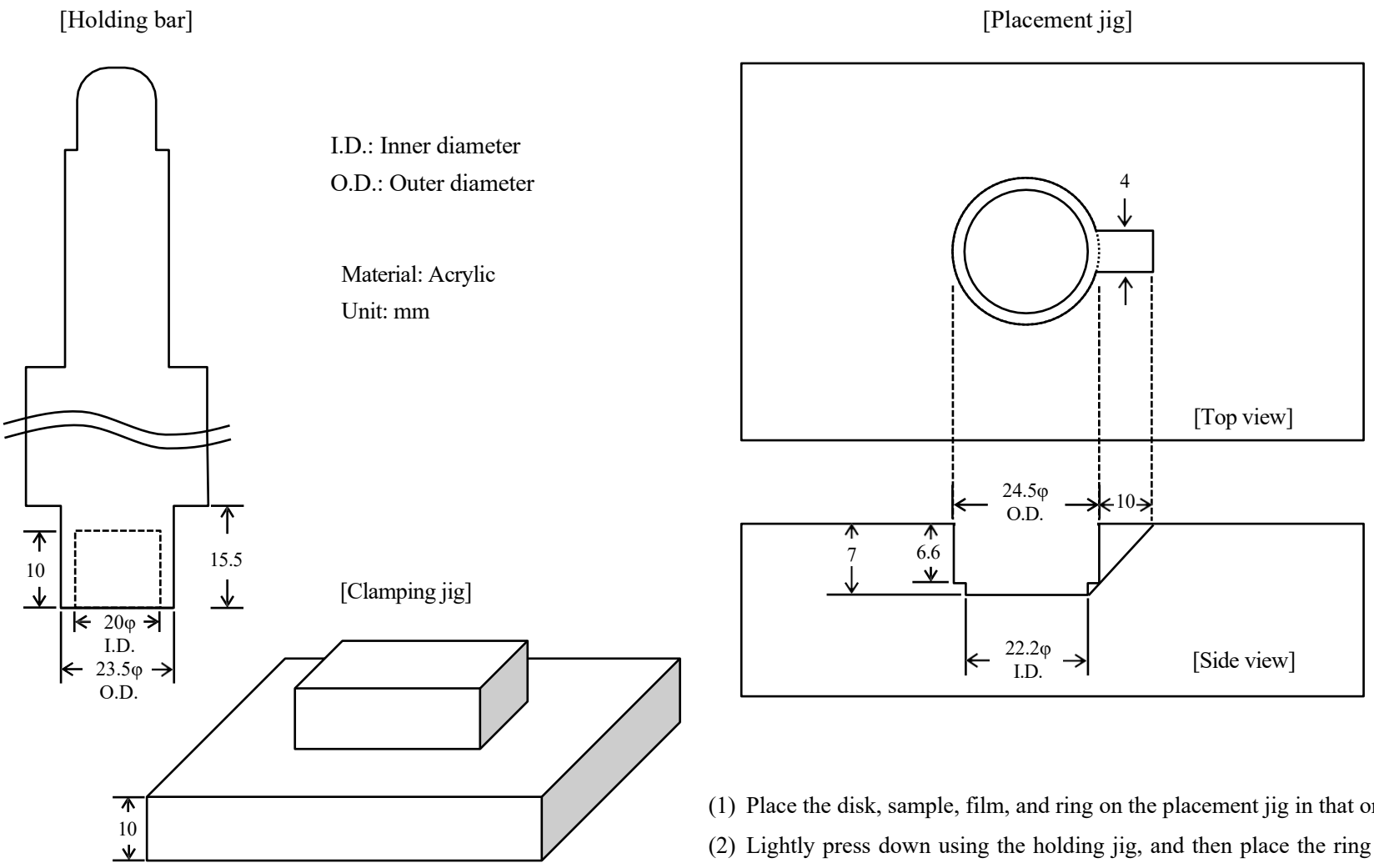
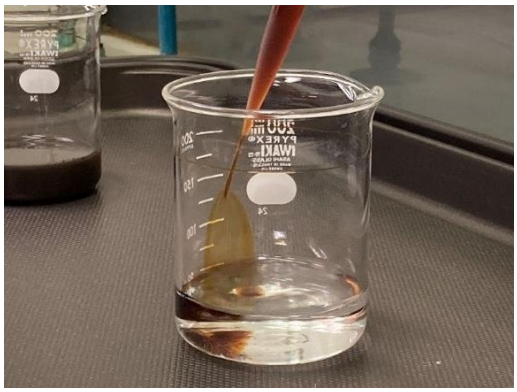



Figure I.1.4 Mounting apparatus

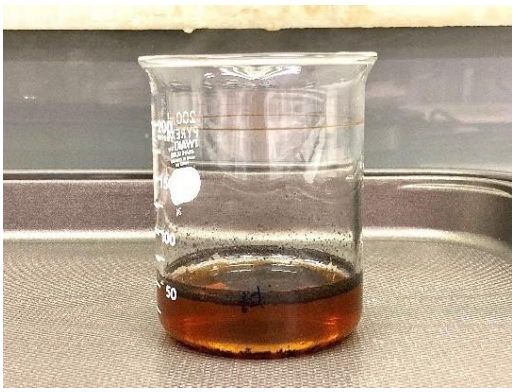



(1) Place the disk, sample, film, and ring on the placement jig in that order.
(2) Lightly press down using the holding jig, and then place the ring into the placement jig.
(3) Use the holding bar to firmly hold the ring and fit it into place.

Figure I.1.5 Holding jig during mounting



(1) Add the palladium chloride solution to the sample.



(2) Heat until boiling to produce a precipitate.



(3) Precipitation of palladium iodide

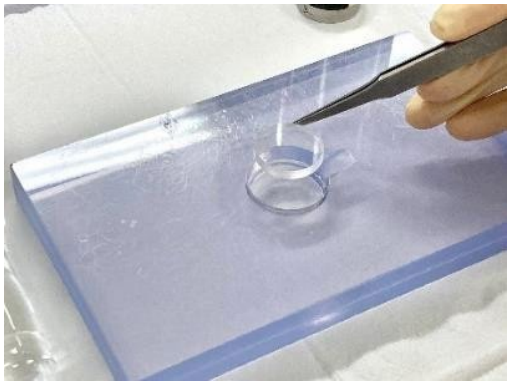


(4) Perform suction filtration.

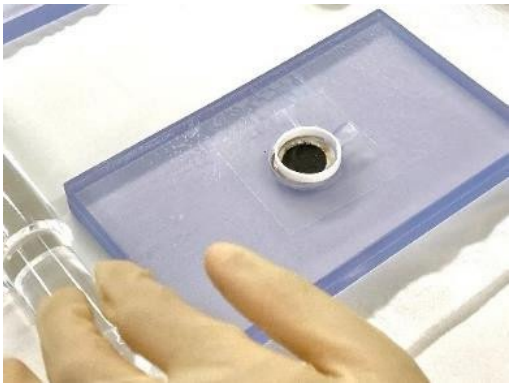


(5) Precipitate
After precipitation, dry the precipitate and the filter paper.

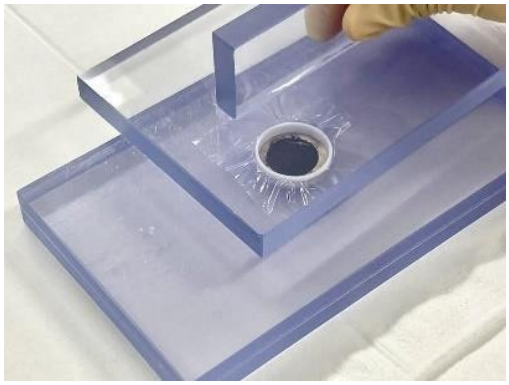
Figure I.1.6 Preparation of the measurement sample (palladium iodide precipitate)



(1) Set the disk.



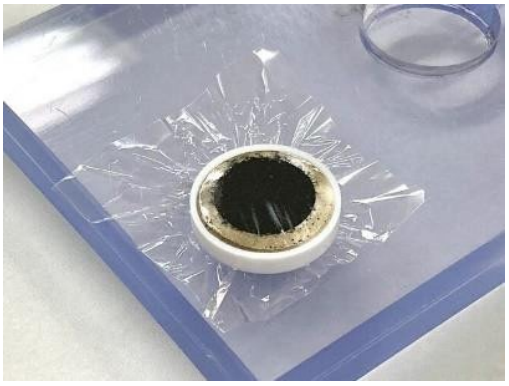
(2) Place the sample, film, and ring in that order.



(3) Lightly press down using the holding jig.



(4) Press down using the holding rod until the ring snaps into place.



(5) Trim off any excess film.



(6) Place on a sample dish.

Figure I.1.7 Mounting apparatus and measurement sample preparation

## 1.3 Combustion–Alkali Solution Absorption Method

### 1.3.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Double-chamber tubular electric furnace (Figure I.1.8)
2) Dryer
3) Balance (weighing range: 0–200 g; readability: ≤0.1 mg)

(2) Instruments

1) Quartz tube (Figure I.1.3)
2) Silicone stopper
3) Quartz wool
4) Gauze
5) Beakers (100 mL and 500 mL)
6) Watch glass (for 100 mL beakers)
7) Gas washing bottle (200 mL)
8) Separatory funnel (100 mL)
9) 1-L pressure bottle
10) Separable filter holder (20 mm diameter)
11) Aspirator
12) Glass funnel (for a 90 mm diameter filter paper)
13) Filter paper
    - Glass-fiber filter paper (90 mm diameter)
    - Separatory filter paper (90 mm diameter)
    - No. 5C filter paper (24 mm diameter)
14) Mounting apparatus
    - Mounting disk (Figure I.1.4)
    - Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/m$^2$)
    - Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
    - Stainless steel sample dish (25 mm diameter)
    - Holding device (Figure I.1.5)
15) Micropipette (1 mL and 5 mL)
16) Pipette tips (1 mL and 5 mL)
17) Desiccator
18) Hot plate

(3) Reagents

1) Nitric acid[*21,*22,*23] (mass fraction: 60%–61% (approximately 13 mol/L); density: 1.38 g/mL)
2) Potassium hydroxide[*22,*23]
   ・Potassium hydroxide (granules)
   ・Potassium hydroxide solution (5 w/v%)
3) Potassium sulfite
   ・Potassium sulfite (granules)
   ・Potassium sulfite solution (10 w/v%)
4) Potassium sulfite solution (10 w/v%)
5) Palladium chloride solution (10 mgPd/mL)
6) Iodine carrier solution (20 mgI/mL)
7) Xylene[*22,*23,*24,*25]
8) Pure water (purified by ion exchange or similar processes)
9) Activated carbon
10) Copper oxide[*22] (needle-shaped)
11) Gases
   ・Oxygen gas (purity ≥ 99.999%)
   ・Nitrogen gas (purity ≥ 99.99%)

### 1.3.2 Analytical Operations

(1) Pretreatment

Perform the same operation as in "(1) Pretreatment" in "1.2 Combustion–Activated Carbon Adsorption Method."

(2) Combustion of samples

1) Prepare two 200 mL gas washing bottles[*26]. Use one as the first-stage bottle. Add 180 mL of pure water, 10 g of potassium hydroxide, and 1 g of potassium sulfite in it. Use the other

[*21] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*22] Substances subject to labeling requirements under the Industrial Safety and Health Act (those posing a significant risk of harm or health impairment to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*23] 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." Further, necessary measures must be implemented to prevent theft, loss, leakage, or other incidents.

[*24] Class II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as the installation of local exhaust ventilation systems, must be implemented.

[*25] Guidelines for preventing health hazards caused by chemical substances, established by the Ministry of Health, Labour and Welfare in accordance with the provisions of Article 28, Paragraph 3 of the Industrial Safety and Health Act, apply. Measures must be implemented to reduce exposure to target substances.

[*26] During sample heating, the temperature of the washing bottle increases; therefore, it should be wrapped using gauze or similar material and maintained in a moistened state using water at all times.

as the second-stage bottle. Add 90 mL of pure water, 5 g of potassium hydroxide, and 0.5 g of potassium sulfite in it. (Refer to Figure I.1.8 while performing the procedure.)

2) Quartz wool wrapped around needle-shaped copper oxide is packed into the section located at the central part of the outer tube of Electric Furnace (B). It serves as a catalyst.
3) Attach the outer tube to the combustion device and install the inner tube inside the outer tube.
4) Supply nitrogen gas to the inner tube at a flow rate of 100 mL/min. Supply oxygen gas to the outer tube at a flow rate of 200 mL/min.
5) Set the temperature of Electric Furnace (B) to 1000°C.
6) Position Electric Furnace (A) at the right edge of the sample and set the temperature to 240°C.
7) While monitoring the tar generation and carbonization conditions, gradually move Electric Furnace (A) to the left. Maintain a constant flow rate of oxygen and nitrogen gases.
8) Once Electric Furnace (A) has moved until it touches Electric Furnace (B), raise the temperature of Electric Furnace (A) to 280°C and continue combustion for ~1 hour. If combustion becomes very intense, lower the temperature.
9) If combustion is stable, raise the temperature of Electric Furnace (A) to 350°C to drive combustible components out of the sample and achieve complete combustion in Electric Furnace (B). Maintain this state for 2–3 hours. The time required to reach 350°C varies depending on the sample condition. Increase the temperature while monitoring combustion and avoiding pressure buildup inside the quartz tube.
10) Once the combustible components are burned, move Electric Furnace (A) to the far right end of the sample.
11) Set the temperature of Electric Furnace (A) to 400°C, supply oxygen gas to the inner tube at a rate of 50 mL/min, and combust the carbonized sample.
12) Gradually move Electric Furnace (A) toward Electric Furnace (B) while reducing the nitrogen-gas flow rate in the inner tube.
13) While monitoring the combustion state, raise the temperature of Electric Furnace (A) to 600°C. If combustion becomes very intense, lower the temperature.
14) Supply oxygen gas through the inner tube at a rate of 100 mL/min and continue combustion.
15) After Electric Furnace (A) has reached Electric Furnace (B), raise the temperature to 1,000°C and completely combust the sample. When tar accumulates at the outlet of the inner pipe, combustion may temporarily intensify; hence, monitor the combustion while raising the temperature.
16) After combustion is complete, turn off the electric furnace switches and remove the washing bottles.
17) Transfer the solutions that have absorbed iodine from the first and second stages in a 500 mL beaker. Rinse the inside of the washing bottle with the potassium hydroxide solution (5 w/v%) and transfer it in a 500 mL beaker.

(3) Chemical separation of iodine after combustion

1) Heat the solution that has absorbed iodine on a hot plate to concentrate it to ~50 mL. After

cooling, transfer the solution in a 100 mL separatory funnel with 20 mL of xylene.

2) While stirring the solution by rotating the separatory funnel, add ~18 mL of nitric acid to adjust the pH to 1[*27].
3) Gradually add 5 mL of the potassium nitrite solution[*28] (10 w/v%) to the mixture. Shake the separatory funnel vigorously for 2 minutes while releasing gases[*29].
4) After allowing it to settle, transfer the aqueous phase in a new 100 mL separatory funnel with 20 mL of xylene. Transfer the organic phase in a separate 100 mL separatory funnel while filtering (using a 90 mm diameter filter paper and glass funnel).
5) Shake the separatory funnel containing the aqueous phase vigorously for 2 minutes. After settling, discard the aqueous phase. Transfer the organic phase to the separatory funnel containing the organic phase mentioned in Step 4 while filtering (using a 90 mm diameter separatory funnel paper and glass funnel).
6) Add 20 mL of pure water and shake vigorously for 2 minutes to wash the organic phase. Then, discard the aqueous phase.
7) Add 20 mL of pure water and 0.5 mL of the potassium sulfite solution[*30] (10 w/v%) to a separatory funnel. Shake vigorously for 2 minutes while occasionally releasing gases[*31].
8) Transfer the aqueous phase to a 100 mL beaker. Leave the organic phase in the separatory funnel and add 20 mL of pure water.
9) Shake the separatory funnel vigorously for 2 minutes while occasionally releasing gases.
10) Transfer the aqueous phase to the 100 mL beaker from Step 8. Discard the organic phase.
11) Cover the beaker with a watch glass and heat it on a hot plate until xylene has completely evaporated. After cooling, add 3 mL of the palladium chloride solution (10 mgPd/mL) and heat to boiling. (Refer to Figure I.1.6 while performing the operation.)
12) After cooling, suction-filter the precipitate (using a filter paper of known weight (No. 5C; 24 mm diameter), a separable filter holder, and a pressure bottle). Discard the filtrate.
13) Dry the precipitate together with the filter paper in a drying oven at 80°C for 1 hour, and then cool it in a desiccator for 30 minutes. Measure the weight of the precipitate.
14) Place the precipitate with the filter paper onto the mounting disk, cover it with a PET film, and secure it using a ring. Trim the film protruding from the ring, transfer it to the sample dish, and use it as the measurement sample. (Refer to Figures I.1.5 and I.1.7 while performing the operation.)

[*27] Verify using a pH test paper.
[*28] Oxidize $I^-$ to $I_2$.
[*29] The organic phase changes from colorless to pink.
[*30] Reduce $I_2$ to $I^-$.
[*31] The organic phase changes from pink to colorless.

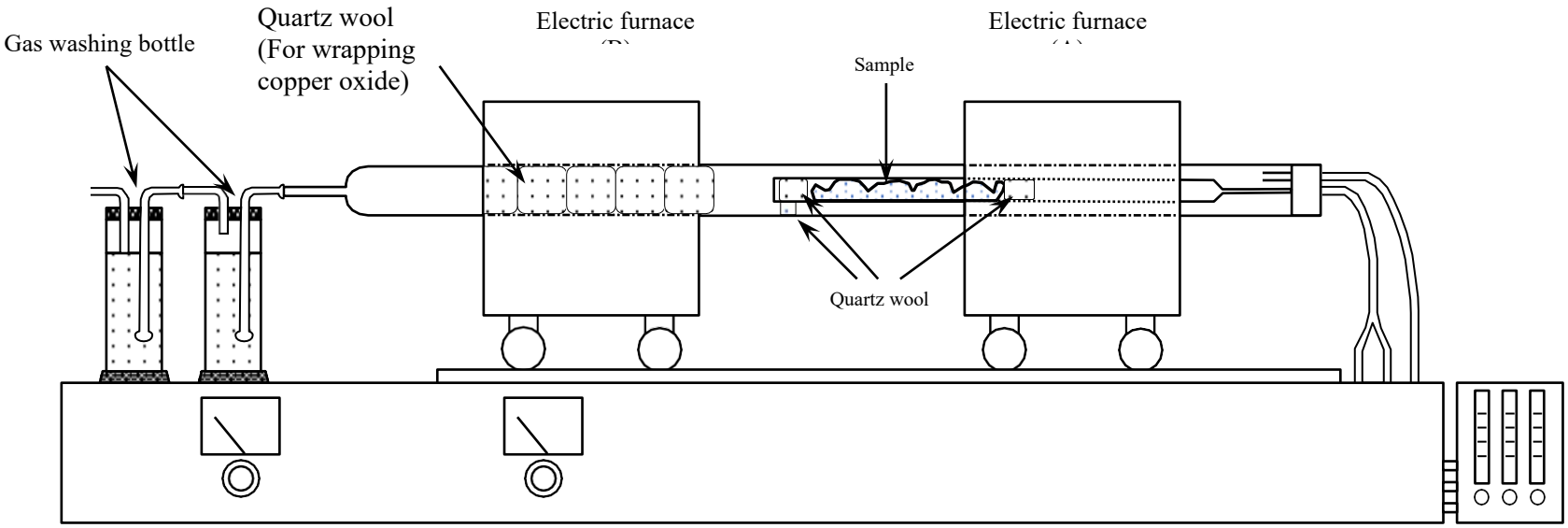



Figure I.1.8 Double-chamber tubular electric furnace

# Chapter 2 Inland Water and Milk

When analyzing inland water and milk samples, iodine in the samples is adsorbed onto an anion-exchange resin and separated and purified by combustion or sodium hypochlorite elution. Combustion methods include the activated-carbon adsorption method and alkali-solution absorption method.

Note that the amount of $^{127}I$[*32,*33] in inland water and milk samples is low. Because 20 mg of an iodine carrier is added prior to analysis, the impact of this addition on the recovery rate of iodine in the sample is <5%. Therefore, $^{127}I$ in the sample is not quantified.

## 2.1 Preparation of Reagents and Resins

The following text describes the preparation methods for reagents and anion-exchange resins used in the radiochemical analysis of inland waters and milk. Reagents should be of the JIS Special Grade. Unless otherwise specified, commercially available products should be used as is. Notably, "pure water" used here refers to water purified by ion exchange or similar processes.

### 2.1.1 Preparation of Reagents

(1) Acids

1) Sulfuric acid (1 + 1): Mix equal parts of 95% sulfuric acid[*34,*35,*36] and pure water.
2) Hydrochloric acid (1 + 1): Mix equal parts of 36% hydrochloric acid[*34,*35,*36] and pure water.

(2) Bases

1) Sodium hydroxide solution
   - Sodium hydroxide solution (24 w/v%): Dissolve 24 g of sodium hydroxide[*35,*36] in 100 mL of pure water.
   - Sodium hydroxide solution (10 w/v%): Dissolve 10 g of sodium hydroxide in 100 mL of pure water.
2) Potassium hydroxide solution (5 w/v%): Dissolve 5 g of potassium hydroxide[*35,*36] in 100 mL of pure water.

[*32] The amount of $^{127}I$ contained in 5 L of inland waters does not exceed ~0.05 mg.
[*33] The amount of $^{127}I$ contained in 5 L of milk does not exceed ~1 mg.
[*34] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures must be implemented to reduce exposure concentrations, such as by installing local exhaust ventilation systems.
[*35] Substances subject to labeling requirements under the Industrial Safety and Health Act (those posing a significant risk of harm or health impairment to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.
[*36] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

(3) Other solutions

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*36,*37] in 100 mL of pure water.
2) Potassium nitrite solution (10 w/v%): Dissolve 10 g of potassium nitrite[*35,*36] in 100 mL of pure water.
3) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of pure water.
4) Potassium sulfite solution (10 w/v%): Dissolve 10 g of potassium sulfite in 100 mL of pure water.
5) Hydroxylamine hydrochloride solution (7 w/v%): Dissolve 7 g of hydroxylamine hydrochloride[*36,*38] in 100 mL of pure water.
6) Palladium chloride solution (10 mgPd/mL): Add 1.7 g of palladium chloride to 50 mL of pure water and 5 mL of hydrochloric acid, followed by heating. After cooling, filter the product (using the No. 5C filter paper). Then, add pure water to the filtrate so that the final volume is 100 mL. (Refer to Figure I.1.1 while performing the operation.)
7) Iodine carrier solution (20 mgI/mL): Dry approximately14 g of sodium iodide at 110°C for 3 hours. Then, cool it in a desiccator for 1 hour. Weigh 11.812 g of the product accurately and dissolve it in 50 mL of pure water. Transfer the resulting solution in a brown 500 mL volumetric flask containing 0.2 mL of the sodium hydroxide solution (24 w/v%) and 1 mL of the sodium sulfite solution (10 w/v%). Then, add pure water up to the mark on the volumetric flask. Finally, store the flask in a cool, dark place.

(4) Other items

1) Anion-exchange resin: Strong-base anion-exchange resin (crosslinking degree: 8%; 50–100 mesh; Cl type)

### 2.1.2 Preparation of Resins

Prepare the resin before use.

(1) Instruments

1) Beakers (1 L, 2 L, and 3 L)
2) Watch glass (for 3 L beakers)
3) Glass rod
4) Anion-exchange resin

(2) Reagents

1) Sodium hydroxide solution (10 w/v%)
2) Hydrochloric acid (1 + 1)
3) Pure water (purified by ion exchange or similar processes)

[*37] Classified as a Class 1 Hazardous Material (Oxidizing Solid) under the Fire Service Act. Avoid contact with strong acids; store away from combustible materials; and prevent heating, impact, or friction.
[*38] Classified as a Class 5 Hazardous Material (Self-reactive Substance) under the Fire Service Act. Avoid heat, impact, and friction. Keep away from combustible materials. Do not allow contact with other chemicals. Store in a cool, dark place.

(3) Procedure

1) Place 500 mL of the resin in a 3 L beaker, add 2 L of pure water, stir thoroughly, and then discard the supernatant by decantation. Repeat this procedure three times.
2) Add 1 L of the sodium hydroxide solution (10 w/v%) and stir thoroughly. Then, remove the supernatant by decantation.
3) Add 2 L of pure water, stir thoroughly, and then remove the supernatant by decantation. Repeat this procedure until the pH of the supernatant reaches 7.
4) Add 2 L of hydrochloric acid (1 + 1) and stir thoroughly. Then, remove the supernatant by decantation.
5) Add 2 L of pure water, stir thoroughly, and then remove the supernatant by decantation. Repeat this procedure until the pH of the supernatant reaches 7. Store while submerged in pure water.

## 2.2 Combustion–Activated Carbon Adsorption Method

### 2.2.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Three-chamber tubular electric furnace (Figure I.1.2)
2) Dryer
3) Balance (weighing range: 0–200 g; readability: ≤0.1 mg)

(2) Instruments

1) Quartz tube (Figure I.1.3)
2) Silicone stopper
3) Quartz wool
4) Anion-exchange resin (prepare according to "2.1.2 Preparation of Resins")
5) Graduated cylinder (5 L)
6) Glass rod
7) Beakers (100 mL, 500 mL, and 5 L)
8) Watch glass (for 100 mL beakers)
9) Erlenmeyer flask (50 mL)
10) Air cooling tube (approximately 30 cm in length; to be attached to a 50 mL Erlenmeyer flask)
11) Separatory funnel (100 mL)
12) 1-L pressure bottle
13) Separable filter holder (for 20 mm diameter and 42 mm diameter filters)
14) Aspirator
15) Glass funnel (for a 90 mm diameter filter paper)
16) Filter paper
    - Glass-fiber filter paper (47 mm diameter)
    - Separatory filter paper (90 mm diameter)
    - No. 5C filter paper (24 mm diameter)
17) Mounting apparatus
    - Mounting disk (Figure I.1.4)
    - Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/$m^2$)
    - Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
    - Stainless steel sample dish (25 mm diameter)
    - Holding device (Figure I.1.5)
18) Micropipette (1 mL and 5 mL)
19) Pipette tips (1 mL and 5 mL)
20) Hand burner (for city gas or propane gas)
21) Desiccator
22) Hot plate

(3) Reagent

1) Nitric acid[*39,*40,*41] (mass fraction: 60–61% (~13 mol/L); density: 1.38 g/mL)
2) Sodium hydroxide solution (24 w/v%)
3) Sodium nitrite solution (10 w/v%)
4) Sodium sulfite solution (10 w/v%)
5) Palladium chloride solution (10 mgPd/mL)
6) Iodine carrier solution (20 mgI/mL)
7) Xylene[*40,*41,*42,*43]
8) Pure water (purified by ion exchange or similar processes)
9) Activated carbon
10) Copper oxide[*40] (needle-shaped)
11) Gases
    - Oxygen gas (purity ≥ 99.999%)
    - Nitrogen gas (purity ≥ 99.99%)
    - City gas or propane gas

### 2.2.2 Analytical Operations

(1) Adsorption onto the anion-exchange resin

1) Measure 5 L of inland water or milk using a graduated cylinder and transfer it in a 5 L beaker.
2) Add 1 mL of the iodine carrier solution (20 mgI/mL) and 0.5 mL of the sodium sulfite solution (10 w/v%).
3) Add 50 mL of prepared anion-exchange resin, stir for 30 minutes using a stirrer, and allow the mixture to settle for 30 minutes.
4) Transfer the inland water or milk to a new 5 L beaker while ensuring that the ion-exchange resin does not spill out during decantation. Transfer the ion-exchange resin to a 500 mL beaker.
5) Add 50 mL of the anion-exchange resin to the inland water or milk, stir for 30 minutes, and allow the mixture to settle for 30 minutes. Discard the inland water or milk while ensuring that the ion-exchange resin does not spill out during decantation. Adjust the ion-exchange resin to 500 mL beaker in Step 4.

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[*39] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, should be implemented.

[*40] Substances subject to labeling requirements under the Industrial Safety and Health Act (those posing potential hazards or health risks to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*41] 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." Further, necessary measures must be implemented to prevent theft, loss, leakage, or other incidents.

[*42] Class II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, should be implemented.

[*43] Guidelines for preventing health hazards caused by chemical substances, established by the Ministry of Health, Labour and Welfare in accordance with the provisions of Article 28, Paragraph 3 of the Industrial Safety and Health Act, apply. Measures must be undertaken to reduce exposure to target substances.

6) Add 300 mL of pure water heated to ~70°C in the resin, stir for several seconds, and then allow the mixture to settle. After the resin precipitates, remove the supernatant by decantation. Repeat this process until the washing solution becomes clear.

(2) Combustion of the anion exchange resin

1) Dry the anion-exchange resin in a dryer at 70°C until it is only slightly moist.
2) Perform the same operation as in "(2) Combustion of samples" in "1.2 Combustion–Activated Carbon Adsorption Method" mentioned in "Chapter 1 Airborne Particulate Matter"[*44].

(3) Chemical separation of iodine after combustion

Perform the same operation as in "(3) Chemical separation of iodine after combustion" in "1.2 Combustion–Activated Carbon Adsorption Method" mentioned in "Chapter 1 Airborne Particulate Matter."

## 2.3 Combustion–Alkali Solution Absorption Method

### 2.3.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Double-chamber tubular electric furnace (Figure I.1.8)
2) Dryer
3) Balance (weighing range: 0–200 g; readability: ≤0.1 mg)

(2) Instruments

1) Quartz tube (Figure I.1.2)
2) Silicone stopper
3) Quartz wool
4) Gauze
5) Anion-exchange resin (prepared according to "2.1.2 Preparation of Resins")
6) Graduated cylinder (5 L)
7) Glass rod
8) Beakers (100 mL, 500 mL, and 5 L)
9) Watch glass (for 100 mL beakers)
10) Gas washing bottle (200 mL)
11) Separatory funnel (100 mL)
12) 1-L pressure bottle

[*44] Quartz wool containing needle-shaped copper oxide is packed into the section of the quartz outer tube located within the electric furnace to enhance the combustion efficiency of the sample. In this case, the combustion of the ion-exchange resin is extremely intense and difficult to control (gases generated from the resin components can cause pressure to increase within the quartz tube). Therefore, it is important to spread the ion-exchange resin thinly within the inner tube, initially supply nitrogen gas only through the inner tube and oxygen gas only through the outer tube, and ensure complete carbonization.

13) Separable filter holder (for 20 mm diameter and 42 mm diameter filters)
14) Aspirator
15) Glass funnel (for a 90 mm diameter filter paper)
16) Filter paper
    ・Glass-fiber filter paper (90 mm diameter)
    ・Separatory filter paper (90 mm diameter)
    ・No. 5C filter paper (24 mm diameter)
17) Mounting apparatus
    ・Mounting disk (Figure I.1.4)
    ・Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/$m^2$)
    ・Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
    ・Stainless steel sample dish (25 mm diameter)
    ・Holding device (Figure I.1.5)
18) Micropipette (1 mL and 5 mL)
19) Pipette tips (1 mL and 5 mL)
20) Desiccator
21) Hot plate

(3) Reagent
1) Nitric acid[*45,*46,*47] (mass fraction: 60%–61% (~13 mol/L); density: 1.38 g/mL)
2) Potassium hydroxide[*46,*47]
    ・Potassium hydroxide (granules)
    ・Potassium hydroxide solution (5 w/v%)
3) Potassium sulfite
    ・Potassium sulfite (granules)
    ・Potassium sulfite solution (10 w/v%)
4) Potassium sulfite solution (10 w/v%)
5) Palladium chloride solution (10 mgPd/mL)
6) Iodine carrier solution (20 mgI/mL)

[*45] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, should be implemented.
[*46] Substances subject to labeling requirements under the Industrial Safety and Health Act (those posing potential hazards or health risks to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.
[*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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

7) Xylene[*46,*47,*48,*49]
8) Pure water (purified by ion exchange or similar processes)
9) Activated carbon
10) Copper oxide[*46] (needle-shaped)
11) Gases
    ・Oxygen gas (purity ≥ 99.999%)
    ・Nitrogen gas (purity ≥ 99.99%)

### 2.3.2 Analytical Operations

(1) Adsorption onto the anion-exchange resin

Perform the same operation as in "(1) Adsorption onto the anion-exchange resin" in "2.2 Combustion–Activated Carbon Adsorption Method."

(2) Combustion of the anion-exchange resin

1) Dry the anion-exchange resin in a dryer at 70°C until it is only slightly moist.
2) Perform the same operation as in "(2) Combustion of samples" in "1.3 Combustion–Alkali Solution Absorption Method" described in "Chapter 1 Airborne Particulate Matter"[*50].

(3) Chemical separation of iodine after combustion

Perform the same operation as in "(3) Chemical separation of iodine after combustion" in "1.3 Combustion–Alkali Solution Absorption Method" described in "Chapter 1 Airborne Particulate Matter."

[*48] Class II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*49] Guidelines for preventing health hazards caused by chemical substances, established by the Ministry of Health, Labour and Welfare in accordance with the provisions of Article 28, Paragraph 3 of the Industrial Safety and Health Act, apply. Measures must be undertaken to reduce exposure to target substances.

[*50] The combustion of ion-exchange resin is extremely intense and difficult to control (gases generated from the resin components can cause pressure to increase within the quartz tube); hence, the ion-exchange resin must be spread thinly on the inner tube.

## 2.4 Sodium Hypochlorite Elution Method

### 2.4.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Balance (weighing range: 0–100 g; readability: ≤0.01 mg)

(2) Instruments

1) Anion-exchange resin (prepared according to "2.1.2 Preparation of Resins")
2) Graduated cylinder (5 L)
3) Glass rod
4) Beakers (100 mL, 300 mL, and 5 L)
5) Watch glass (for 100 mL beakers)
6) Separatory funnel (100 mL and 500 mL)
7) 1 L pressure bottle
8) Separable filter holder (for 20 mm diameter filter papers)
9) Aspirator
10) Glass funnel (for 90 mm diameter filter paper)
11) Filter paper
    - Glass-fiber filter paper (90 mm diameter)
    - Separatory filter paper (90 mm diameter)
    - No. 5C filter paper (24 mm diameter)
12) Mounting apparatus
    - Mounting disk (Figure I.1.4)
    - Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/$m^2$)
    - Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
    - Stainless steel sample dish (25 mm diameter)
    - Holding device (Figure I.1.5)
13) Micropipette (1 mL and 5 mL)
14) Pipette tips (1 mL and 5 mL)
15) Desiccator
16) Hot plate

(3) Reagents

1) Nitric acid[*51,*52,*53] (mass fraction: 60%–61% (approximately 13 mol/L), density: 1.38 g/mL)
2) Sulfuric acid[*51,*52,*53] (1 + 1)
3) Sodium hypochlorite solution (5% available chlorine)
4) Hydroxylamine hydrochloride solution (7 w/v%)
5) Palladium chloride solution (10 mgPd/mL)
6) Iodine carrier solution (20 mgI/mL)
7) Xylene[*52,*53,*54,*55]
8) Pure water (purified by ion exchange or similar processes)

### 2.4.2 Analytical Operations

(1) Adsorption onto the anion-exchange resin

Perform the same operation as in "(1) Adsorption onto the anion-exchange resin" in "2.2 Combustion–Activated Carbon Adsorption Method."

(2) Elution from the anion-exchange resin

1) Add 100 mL of the sodium hypochlorite solution[*56] (5% available chlorine) to the cleaned resin and stir for 5 minutes.
2) Suction-filter the resin using a 3G glass filter and pressure bottle.
3) Transfer the ion-exchange resin in a new 300 mL beaker and the filtrate in a new 500 mL beaker.
4) Add 100 mL of the sodium hypochlorite solution to the ion-exchange resin mentioned in Step 3 and stir using a stirrer for 5 minutes.
5) Suction-filter the resin using a 3G glass filter and pressure bottle. Adjust the filtrate to 500 mL beaker in Step 3. Discard the resin.
6) Stir using a glass rod while adding sulfuric acid (1 + 1)[*57], adjusting the solution pH to 1. Stir until no more bubbles form in the solution.

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[*51] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*52] Substances subject to hazardous substance labeling under the Industrial Safety and Health Act (those posing potential risks or health hazards to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*53] 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." Further, necessary measures must be taken to prevent theft, loss, leakage, or other incidents.

[*54] Class II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*55] Guidelines for preventing health hazards caused by chemical substances, established by the Ministry of Health, Labour and Welfare in accordance with the provisions of Article 28, Paragraph 3 of the Industrial Safety and Health Act, apply. Measures must be undertaken to reduce exposure to target substances.

[*56] Oxidize $I^-$ to $IO_3^-$.

[*57] Since a large amount of chlorine is generated, this operation must be performed in a fume hood.

7) While stirring the solution using a glass rod, add 48 mL of sulfuric acid (1 + 1) and heat on a hot plate to thoroughly expel generated chlorine.

(3) Chemical separation of iodine after elution

1) After allowing the solution from which sufficient chlorine has been expelled to cool to room temperature, add pure water so that the final volume is 400 mL and transfer the solution to a 500 mL separatory funnel.
2) Add 50 mL of xylene[*58]. Occasionally release gases while vigorously shaking for 1 minute. Transfer the aqueous phase to a new 500 mL separatory funnel and discard xylene[*59].
3) Add 50 mL of xylene and 5 mL of the hydroxylamine hydrochloride solution (7 w/v%). Seal the container, gently shake the solution to mix it, and let it stand for 10 minutes.
4) Shake the separatory funnel vigorously for 2 minutes while releasing gases[*60]. Transfer the aqueous phase to a new 500 mL separatory funnel.
5) Transfer the organic phase to a 500 mL separatory funnel containing 100 mL of pure water while filtering (using a 90 mm diameter separatory filter paper and a glass funnel).
6) Add 50 mL of xylene and 0.2 mL of the hydroxylamine hydrochloride solution (7 w/v%) in the separatory funnel containing the aqueous phase mentioned in Step 4.
   Seal the funnel, gently shake the solution to mix it, and let it stand for 2 minutes.
7) Shake the separatory funnel vigorously for 2 minutes while releasing gases. Discard the aqueous phase.
8) Transfer the organic phase to a separatory funnel containing the organic phase mentioned in Step 5 while filtering it (using a 90 mm diameter separatory filter paper and a glass funnel).
9) Shake the separatory funnel vigorously for 2 minutes to wash the organic phase. Discard the aqueous phase.
10) Add 50 mL of pure water and 0.5 mL of the sodium sulfite solution[*61] (10 w/v%) to a separatory funnel. Shake vigorously for 2 minutes while occasionally releasing gases[*62].
11) Transfer the aqueous phase to a 200 mL beaker. Leave the organic phase in the separatory funnel and add 50 mL of pure water.
12) Shake vigorously for 2 minutes while occasionally releasing gases.
13) Combine the aqueous phase with the contents of the beaker mentioned in Step 11. Discard the organic phase.
14) Cover the beaker with a watch glass and heat it on a hot plate until xylene evaporates completely. After cooling, add 3 mL of the palladium chloride solution (10 mgPd/mL) and heat to boiling. (Refer to Figure I.1.4 while performing the operation.)

[*58] In addition to xylene, benzene and toluene can be used. However, care must be taken to ensure safety during their use. Examples of iodine recovery rates obtained using different organic solvents are 91% (xylene), 99% (benzene), and 84% (toluene).
[*59] This operation is performed to remove any remaining chlorine.
[*60] The organic phase changes from colorless to pink.
[*61] Reduce $I_2$ to $I^-$.
[*62] The organic phase changes from pink to colorless.

15) After cooling, suction-filter the precipitate (using a filter paper of known weight (No. 5C; 24 mm diameter), a separable filter holder, and a pressure bottle). Discard the filtrate.
16) Dry the precipitate together with the filter paper in a drying oven at 80°C for 1 hour. Allow it to cool for 30 minutes in a desiccator, and then weigh the precipitate.
17) Place the precipitate with the filter paper onto the mounting disk, cover with a PET film, and secure it with a ring. Trim any film protruding from the ring, transfer it to the sample dish, and use it as the measurement sample. (Refer to Figures I.1.5 and I.1.7 while performing the operation).

# Chapter 3 Seawater

When analyzing seawater samples, iodine is recovered using silver nitrate and then separated and purified via solvent extraction.

The amount of $^{127}I$ in seawater is low. Since 20 mg of an iodine carrier is added before analysis, its effect on the recovery rate of iodine in the sample is <5%. Therefore, $^{127}I$ in the sample is not quantified.

## 3.1 Preparation of Reagents

The following text describes the preparation methods for reagents used in the radiochemical analysis of seawater. Reagents should be of the JIS Special Grade. Unless otherwise specified, commercially available products should be used as is. "Pure water" mentioned here refers to water purified by ion exchange or similar processes.

(1) Acids

1) Nitric acid (1 + 6): Mix 1 part 60% nitric acid[*63,*64,*65] with 6 parts pure water.
2) Sulfuric acid (1 + 5): Mix 1 part 95% sulfuric acid[*63,*64,*65] with 5 parts pure water.

(2) Bases

1) Sodium hydroxide solution (24 w/v%): Dissolve 24 g of sodium hydroxide[*64,*65] in 100 mL of pure water.

(3) Other solutions

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*65,*66] in 100 mL of pure water.
2) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of pure water.
3) Saturated hydrazinium sulfate solution: Use the supernatant obtained by dissolving 5 g of hydrazinium sulfate[*64,*67] in 100 mL of pure water.
4) Silver nitrate solution (0.3 w/v%): Dissolve 0.3 g of silver nitrate[*64,*65] in 100 mL of pure water.

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*63 Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

*64 Substances subject to labeling requirements under the Industrial Safety and Health Act (those posing potential hazards or health risks to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

*65 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." Further, necessary measures must be taken to prevent theft, loss, leakage, or other incidents.

*66 Classified as a Class 1 Hazardous Material (Oxidizing Solid) under the Fire Service Act. Avoid contact with strong acids; store away from combustible materials; and prevent heating, impact, or friction.

*67 Classified as a Class 5 Hazardous Material (Self-reactive Substance) under the Fire Service Act. Avoid heat, impact, and friction. Keep away from combustible materials. Do not allow contact with other chemicals. Store in a cool, dark place.

5) Palladium chloride solution (10 mgPd/mL): Add 1.7 g of palladium chloride to 50 mL of pure water and 5 mL of hydrochloric acid, followed by heating. Allow the mixture to cool, and then filter it (using the No. 5C filter paper). Add pure water to the filtrate so that the final volume is 100 mL. (Refer to Figure I.1.1 while performing the operation.)
6) Iodine carrier solution (20 mgI/mL): Dry approximately 14 g of sodium iodide[*64] at 110°C for 3 hours. Then, cool it for 1 hour in a desiccator. Weigh 11.812 g and dissolve in 50 mL of pure water. Transfer the solution to a brown 500 mL volumetric flask containing 0.2 mL of the sodium hydroxide solution (24 w/v%) and 1 mL of the sodium sulfite solution (10 w/v%). Then, add pure water up to the mark on the volumetric flask Store in a cool, dark place.

## 3.2 Silver Iodide Precipitation Method

### 3.2.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Balance (weighing range: 0–100 g; readability: ≤0.01 mg)

(2) Instruments

1) Graduated cylinder (5 L)
2) Glass rod
3) Beakers (100 mL, 200 mL, 300 mL, and 5 L)
4) Watch glass (for 100 mL beakers)
5) Separatory funnel (100 mL and 300 mL)
6) 1-L pressure bottle
7) Separable filter holder (for 20 mm diameter filter papers)
8) Aspirator
9) Glass funnel (for a 90 mm diameter filter paper)
10) Büchner funnel (for a 110 mm diameter filter paper)
11) Filter paper
    - Glass-fiber filter paper (90 mm diameter)
    - Separatory filter paper (90 mm diameter and 110 mm diameter)
    - No. 5C filter paper (24 mm diameter and 110 mm diameter)
12) Mounting apparatus
    - Mounting disk (Figure I.1.4)
    - Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/m$^2$)
    - Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
    - Stainless steel sample dish (25 mm diameter)
    - Holding device (Figure I.1.5)
13) Micropipette (1 mL and 5 mL)
14) Pipette tips (1 mL and 5 mL)

15) Desiccator
16) Hot plate

(3) Reagent

1) Nitric acid[*68,*69,*70] (mass fraction: 60–61% (~13 mol/L); density: 1.38 g/mL)
   • Nitric acid (undiluted)
   • Nitric acid (1 + 6)
2) Sulfuric acid (1 + 5)[*68,*69,*70]
3) Sodium hydroxide solution (24 w/v%)
4) Sodium nitrite solution (10 w/v%)
5) Sodium sulfite solution (10 w/v%)
6) Saturated hydrazinium sulfate solution
7) Silver nitrate solution (0.3 w/v%)
8) Palladium chloride solution (10 mgPd/mL)
9) Iodine carrier solution (20 mgI/mL)
10) Xylene[*69,*70,*71,*72]
11) Pure water (purified by ion exchange or similar processes)
12) Powdered zinc

### 3.2.2 Analytical Operations

1) Measure 5 L of seawater using a graduated cylinder and transfer it to a 5 L beaker.
2) Add 1 mL of the iodine carrier solution (20 mgI/mL), 20 mL of sulfuric acid (1 + 5), and 40 mL of the saturated hydrazinium sulfate solution[*73].
3) Stir well and let the mixture stand for 10 minutes.
4) Gradually add 100 mL of the silver nitrate solution (0.3 w/v%) while stirring to produce a silver iodide precipitate.
5) Filter the precipitate (using the No. 5C filter paper (110 mm diameter), a Büchner funnel, and a pressure bottle). Discard the filtrate.

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[*68] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*69] Substances subject to labeling requirements under the Industrial Safety and Health Act (those posing potential hazards or health risks to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*70] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

[*71] Class II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*72] Guidelines for preventing health hazards caused by chemical substances, established by the Ministry of Health, Labour and Welfare in accordance with the provisions of Article 28, Paragraph 3 of the Industrial Safety and Health Act, apply. Measures must be undertaken to reduce exposure to target substances.

[*73] Reduce iodine to $I^-$.

6) Transfer the precipitate along with the filter paper to a 300 mL beaker. Add 50 mL of water, 1 g of zinc powder[*74], and 0.5 mL of sulfuric acid (1 + 5). Then, heat the mixture for 1 minute.
7) Filter the resulting silver metal and excess zinc (using the No. 5C filter paper (110 mm diameter) and a glass funnel). Collect the filtrate in a 200 mL beaker. Discard the residue.
8) Transfer the filtrate to a 300 mL separatory funnel containing 20 mL of xylene.
9) Add 1 mL of nitric acid (1 + 5) and 1 mL of the sodium nitrite solution (10 w/v%)[*75]. Shake vigorously for 2 minutes while occasionally releasing gases[*76]. Transfer the aqueous phase to a new 300 mL separatory funnel.
10) Transfer the organic phase to a 100 mL separatory funnel containing 20 mL of pure water while filtering (using a 90 mm diameter separatory filter paper and a glass funnel).
11) Add 20 mL of xylene to the separatory funnel containing the aqueous phase mentioned in Step 9. Shake the separatory funnel vigorously for 2 minutes while occasionally releasing gases. Discard the aqueous phase.
12) Transfer the organic phase to a separatory funnel containing the organic phase mentioned in Step 10 while filtering it (using a 90 mm diameter separatory filter paper and a glass funnel).
13) Shake the separatory funnel vigorously for 2 minutes to wash the organic phase. Discard the aqueous phase.
14) Add 20 mL of pure water and 0.2 mL of the sodium sulfite solution[*77] (10 w/v%) to a separatory funnel. Shake vigorously for 2 minutes while occasionally releasing gases[*78].
15) Transfer the aqueous phase to a 100 mL beaker. Leave the organic phase in the separatory funnel and add 20 mL of pure water.
16) Shake the separatory funnel vigorously for 2 minutes while occasionally releasing gases.
17) Adjust the liquid phase to the beaker in Step 15. Discard the organic phase.
18) Cover the beaker with a watch glass and heat it on a hot plate until xylene is completely evaporated. After cooling, add 3 mL of the palladium chloride solution (10 mgPd/mL) and heat to boiling.
(Refer to Figure I.1.6 while performing the operation.)
19) After cooling, suction-filter the precipitate (using a filter paper of known weight (No. 5C; 24 mm diameter), a separable filter holder, and a pressure bottle). Discard the filtrate.
20) Dry the precipitate together with the filter paper in a drying oven at 80°C for 1 hour. Then, allow it to cool for 30 minutes in a desiccator. After cooling, weigh the precipitate.
21) Place the precipitate with the filter paper onto the mounting disk, cover with a PET film, and secure it with a ring. Trim any film protruding from the ring, transfer it to the sample dish, and use it as the measurement sample. (Refer to Figures I.1.5 and I.1.7 while performing the operation.)

[*74] Reduce silver and release iodine as $I^-$.
[*75] Oxidize $I^-$ into $I_2$.
[*76] The organic phase changes from colorless to pink.
[*77] Reduce $I_2$ to $I^-$.
[*78] The organic phase changes from pink to colorless.

# Chapter 4 Soil

When analyzing soil samples, iodine separation and purification are carried out using either the activated-carbon adsorption method, wherein soil is combusted and iodine is adsorbed onto activated carbon, or the alkali-solution absorption method, wherein iodine is absorbed into an alkali solution.

Note that since some soils contain high levels of $^{127}I$[*79], when accurate recovery rate correction is required, iodine in the sample should be quantified based on "4.4 Determination of $^{127}I$ in Soil Samples."

This method can also be applied to samples such as seabed soils and marine sediments.

## 4.1 Preparation of Reagents

The following text describes the preparation method for reagents used in the radiochemical analysis of soil samples. Reagents should be of the JIS Special Grade. Unless otherwise specified, commercially available products should be used as is. "Pure water" mentioned here refers to water purified by ion exchange or similar processes.

(1) Bases

1) Sodium hydroxide solution (24 w/v%): Dissolve 24 g of sodium hydroxide[*80,*81] in 100 mL of pure water.
2) Potassium hydroxide solution (5 w/v%): Dissolve 5 g of potassium hydroxide[*80,*81] in 100 mL of pure water.

(2) Other solutions

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*81,*82] in 100 mL of pure water.
2) Potassium nitrite solution (10 w/v%): Dissolve 10 g of potassium nitrite[*81,*82] in 100 mL of pure water.
3) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of pure water.
4) Potassium sulfite solution (10 w/v%): Dissolve 10 g of potassium sulfite in 100 mL of pure water.

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[*79] The amount of $^{127}I$ contained in soil samples varies depending on the sample type and collection site. It typically ranges from 0.1 mg to 4 mg per 100 g of soil. Moreover, it has been reported that the concentration of $^{129}I$ in soil is generally higher in the surface layer than in the subsurface layer.

[*80] Substances subject to hazardous substance labeling under the Industrial Safety and Health Act (those posing potential risks or health hazards to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*81] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

[*82] Classified as Class 1 Hazardous Materials (Oxidizing Solids) under the Fire Service Act. Avoid contact with strong acids; store away from combustible materials; and prevent heating, impact, or friction.

5) Palladium chloride solution (10 mgPd/mL): Add 1.7 g of palladium chloride to 50 mL of pure water and 5 mL of 36% hydrochloric acid[*80,*81,*83], followed by heating. Allow the mixture to cool and then filter it (using the No. 5C filter paper). Add pure water to the filtrate so that the final volume is 100 mL. (Refer to Figure I.1.1 while performing the operation).
6) Iodine carrier solution (20 mgI/mL): Dry ~14 g of sodium iodide[*80] at 110°C for 3 hours. Then, cool it for 1 hour in a desiccator. Weigh 11.812 g and dissolve in 50 mL of pure water. Transfer the solution to a brown 500 mL volumetric flask containing 0.2 mL of the sodium hydroxide solution (24 w/v%) and 1 mL of the sodium sulfite solution (10 w/v%). Then, add pure water up to the mark on the volumetric flask. Store in a cool, dark place.

## 4.2 Combustion–Activated Carbon Adsorption Method

### 4.2.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Three-chamber tubular electric furnace (Figure I.1.2)
2) Dryer
3) Balance (weighing range: 0–200 g; readability: ≤0.1 mg)

(2) Instruments

1) Quartz tube (Figure I.1.3)
2) Silicone stopper
3) Quartz wool
4) Beaker (100 mL)
5) Watch glass (for 100 mL beakers)
6) Erlenmeyer flask (50 mL)
7) Air cooling tube (approximately 30 cm in length; to be attached to a 50 mL Erlenmeyer flask)
8) Separatory funnel (100 mL)
9) 1-L pressure bottle
10) Separable filter holder (for 20 mm diameter and 42 mm diameter filters)
11) Aspirator
12) Glass funnel (for a 90 mm diameter filter paper)
13) Filter paper
    - Glass-fiber filter paper (47 mm diameter)
    - Separatory filter paper (90 mm diameter)
    - No. 5C filter paper (24 mm diameter)
14) Mounting apparatus
    - Mounting disk (Figure I.1.4)

[*83] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

・Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/m$^2$)
・Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
・Stainless steel sample dish (25 mm diameter)
・Holding device (Figure I.1.5)

15) Micropipette: 1 mL, 5 mL
16) Pipette tips (1 mL and 5 mL)
17) Hand burner (for city gas or propane gas)
18) Desiccator
19) Hot plate

(3) Reagent

1) Nitric acid[*84,*85,*86] (mass fraction: 60–61% (approximately 13 mol/L); density: 1.38 g/mL)
2) Sodium hydroxide solution (24 w/v%)
3) Sodium nitrite solution (10 w/v%)
4) Sodium sulfite solution (10 w/v%)
5) Palladium chloride solution (10 mgPd/mL)
6) Iodine carrier solution (20 mgI/mL)
7) Xylene[*85,*86,*87,*88]
8) Pure water (purified by ion exchange or similar processes)
9) Activated carbon
10) Copper oxide[*85] (needle-shaped)
11) Gases
・Oxygen gas (purity ≥ 99.999%)
・Nitrogen gas (purity ≥ 99.99%)
・City gas or propane gas

### 4.2.2 Analytical Operations

(1) Pretreatment

1) Dry the soil sample at approximately 70°C. After pulverization, weigh 100 g[*89] and pack it

[*84] Class III substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*85] Substances subject to hazardous substance labeling under the Industrial Safety and Health Act (those posing potential risks or health hazards to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*86] 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." Further, necessary measures must be implemented to prevent theft, loss, leakage, or other incidents.

[*87] Class II Substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*88] Guidelines for Prevention of Health Hazards from Chemical Substances Designated by the Ministry of Health, Labour and Welfare in accordance with Article 28, Paragraph 3 of the Industrial Safety and Health Act: Measures must be taken to reduce exposure to target substances.

[*89] A single operation can burn up to approximately 100 g.

into the inner tube of the quartz tube (Figure I.1.2)[*90]. When doing so, prepack the narrower end of the inner tube with quartz wool. (Refer to Figure I.1.3 while performing the operation).

2) Add 1 mL of the iodine carrier solution (20 mgI/mL).
3) Seal the ends of the inner tube with quartz wool.

(2) Combustion of samples

1) Fill the narrowed section of the outer tube with quartz wool, add 3 g of activated carbon, and seal the end with quartz wool.
2) Pack quartz wool into the section located at the center of Electric Furnace (B) of the outer tube.
3) Attach the outer tube to the combustion device and install the inner tube inside the outer tube.
4) Set the temperature of Electric Furnace (C) used for activated-carbon insulation to 150°C and the temperature of Electric Furnace (B) to 1000°C.
5) Supply oxygen and nitrogen gases separately to the inner tube at a rate of 50 mL/min. Supply oxygen gas to the outer tube at a rate of 200 mL/min.
6) Position Electric Furnace (A) at the right edge of the sample and set the temperature to 250°C.
7) Gradually move Electric Furnace (A) toward Electric Furnace (B) to expel moisture.
8) After moving Electric Furnace (A) until it touches Electric Furnace (B), move Electric Furnace (A) to the right edge of the sample.
9) Set the temperature of Electric Furnace (A) to 700°C, gradually move the sample toward Electric Furnace (B), and combust the sample.
10) After moving Electric Furnace (A) until it touches Electric Furnace (B), move Electric Furnace (A) to the center of the sample.
11) Set the temperature of Electric Furnace (A) to 1000°C and combust the sample for approximately 2 hours.
12) Set the temperature of Electric Furnace (B) to 500°C and turn off Electric Furnace (A).
13) After sample combustion is complete, pack the narrow section of the trap tube with quartz wool, insert 0.5 g of activated carbon, and seal the end with quartz wool. Connect the trap pipe to the ball joint at the left end of the outer pipe using a clamp. Shift the outer pipe to the right so that the trap pipe aligns with Electric Furnace (C) and the right end of (D) aligns with the left end of Electric Furnace (B). Supply oxygen gas at a rate of mL/min through the outer and inner tubes.
14) Adjust the flow rate of oxygen gas in the inner tube while observing the ignition and combustion state of Activated Carbon (D) and the pressure within the quartz tube. Gradually move Electric Furnace (B) to the left to completely combust the activated carbon.
15) After the activated carbon has finished burning, heat the joint area using a hand burner to burn any remaining tar residue.

[*90] When placing a sample into the inner tube of a quartz tube, failure to ensure a gap for oxygen and nitrogen gases to pass through may prevent proper combustion. Furthermore, when samples contain a high amount of organic matter, sudden combustion reactions may occur during burning; hence, extreme caution is necessary.

(3) Chemical separation of iodine after combustion

Perform the same operation as in "(3) Chemical separation of iodine after combustion" in "1.2 Combustion–Activated Carbon Adsorption Method" described in "Chapter 1 Airborne Particulate Matter."

## 4.3 Combustion–Alkali Solution Absorption Method

### 4.3.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Double-chamber tubular electric furnace (Figure I.1.8)
2) Dryer
3) Balance (weighing range: 0–200 g; readability: ≤0.1 mg)

(2) Instruments

1) Quartz tube (Figure I.1.3)
2) Silicone stopper
3) Quartz wool
4) Gauze
5) Beakers (100 mL and 500 mL)
6) Watch glass (for 100 mL beakers)
7) Gas washing bottle (200 mL)
8) Separatory funnel (100 mL)
9) 1-L pressure bottle
10) Separable filter holder (for 20 mm diameter filters)
11) Aspirator
12) Glass funnel (for a 90 mm diameter filter paper)
13) Filter paper
    - Glass-fiber filter paper (90 mm diameter)
    - Separatory filter paper (90 mm diameter)
    - No. 5C filter paper (24 mm diameter)
14) Mounting apparatus
    - Mounting disk (Figure I.1.4)
    - Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/$m^2$)
    - Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
    - Stainless steel sample dish (25 mm diameter)
    - Holding device (Figure I.1.5)
15) Micropipette (1 mL and 5 mL)
16) Micropipette tips (1 mL and 5 mL)
17) Desiccator
18) Hot plate

(3) Reagent

1) Nitric acid[*91,*92,*93] (mass fraction: 60–61% (~13 mol/L); density: 1.38 g/mL)
2) Potassium hydroxide[*92,*93]
   - Potassium hydroxide (granules)
   - Potassium hydroxide solution (5 w/v%)
3) Potassium sulfite
   - Potassium sulfite (granules)
   - Potassium sulfite solution (10 w/v%)
4) Potassium sulfite solution (10 w/v%)
5) Palladium chloride solution (10 mgPd/mL)
6) Iodine carrier solution (20 mgI/mL)
7) Xylene[*92,*93,*94,*95]
8) Pure water (purified by ion exchange or similar processes)
9) Activated carbon
10) Copper oxide[*92] (needle-shaped)
11) Gases
    - Oxygen gas (purity ≥ 99.999%)
    - Nitrogen gas (purity ≥ 99.99%)

### 4.3.2 Analytical Operations

(1) Pretreatment

Perform the same operation as in "(1) Pretreatment" in "4.2 Combustion–Activated Carbon Adsorption Method."

(2) Combustion of samples

1) Prepare two 200 mL gas washing bottles[*96]. In one bottle, which is to be used in the first stage, add 180 mL of pure water, 10 g of potassium hydroxide, and 1 g of potassium sulfite. The other bottle is to be used in the second stage. Add 90 mL of pure water, 5 g of potassium

[*91] Class III substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*92] Substances subject to hazardous substance labeling under the Industrial Safety and Health Act (those posing potential risks or health hazards to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*93] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

[*94] Class II substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*95] Guidelines for preventing health hazards caused by chemical substances, established by the Ministry of Health, Labour and Welfare in accordance with the provisions of Article 28, Paragraph 3 of the Industrial Safety and Health Act, apply. Measures must be undertaken to reduce exposure to target substances.

[*96] While heating the sample, the temperature of the washing bottle will increase. Wrap the bottle using gauze or a similar material and keep it continuously moistened with water.

hydroxide, and 0.5 g of potassium sulfite in this bottle. (Refer to Figure I.1.8 while performing the procedure).

2) Pack quartz wool into the section of the outer tube located in Electric Furnace (B). Wrap needle-shaped copper oxide, which acts as a catalyst, in quartz wool.
3) Attach the outer tube to the combustion device and install the inner tube in the outer tube.
4) Supply oxygen gas at a rate of 100 mL/min to the inner tube and at a rate of 200 mL/min to the outer tube.
5) Set the temperature of Electric Furnace (B) to 1000°C.
6) Position Electric Furnace (A) at the right edge of the sample, set the temperature to 1000°C, and gradually move it toward Electric Furnace (B) over approximately 2 hours to combust the sample.
7) After combustion is complete, turn off the electric furnaces and remove the washing bottles.
8) Transfer the iodine-absorbed solutions from the first and second stages to a 500 mL beaker. Rinse the interior of the washing bottle with a small amount of the potassium hydroxide solution (5 w/v%) and transfer it to the 500 mL beaker mentioned earlier.

(3) Chemical separation of iodine after combustion

Perform the same operation as in "(3) Chemical separation of iodine after combustion" in "1.3 Combustion–Alkali Solution Absorption Method" described in "Chapter 1 Airborne Particulate Matter."

## 4.4 Determination of $^{127}$I in Soil Samples

Several analytical methods can be used for the quantitative analysis of $^{127}$I. This section describes a method for measuring $^{127}$I using the ion electrode method[*97].

### 4.4.1 Preparation of Reagents

(1) Bases

1) Sodium hydroxide solution (10 w/v%): Dissolve 10 g of sodium hydroxide[*92,*93] in 100 mL of pure water.

(2) Other solutions

1) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of pure water.
2) Phosphonic acid solution (50 w/v%): Mix equal parts of phosphorous acid solution and pure water.

[*97] Other methods available for the quantitative analysis of $^{127}$I include ① ICP mass spectrometry, ② ion chromatography, ③ gravimetric analysis, ④ volumetric analysis, ⑤ spectrophotometry, and ⑥ the contact method.

3) Acetic acid buffer solution: Dissolve 100 g of potassium nitrate[*98] in 25 mL of glacial acetic acid. Add a sodium hydroxide solution (10 w/v%) to adjust the pH to 5. Then, add pure water so that the final volume is 1 L.
4) Iodine solution
   - Iodine carrier solution (20 mgI/mL): Dry approximately 14 g of sodium iodide at 110°C for 3 hours. Then, allow it to cool for 1 hour in a desiccator. Weigh 11.812 g and dissolve in 50 mL of pure water. Transfer the resulting solution to a brown 500 mL volumetric flask containing 0.2 mL of the sodium hydroxide solution (24 w/v%) and 1 mL of the sodium sulfite solution (10 w/v%). Then, add pure water up to the mark on the volumetric flask Store in a cool, dark place.
   - Iodine standard solution (5 $\mu$gI/mL): Dilute the iodine carrier solution (20 mgI/mL) 4000-fold using pure water immediately before use.

### 4.4.2 Analytical Operations

(1) Equipment
1) Distillation apparatus (Figure I.4.1)
2) Ion meter
3) Balance (weighing range: 0–10 g; readability: ≤0.01 mg)

(2) Instruments
1) Distillation flask (300 mL)
2) Beaker (100 mL)
3) Volumetric flask (100 mL)
4) Test tube (30 mL)
5) Komagome pipette (10 mL)
6) Mantle heater
7) Rotor
8) Magnetic stirrer
9) Thermometer (for 200°C)
10) Gas flowmeter
11) Hot plate
12) Micropipettes (1 mL, 5 mL, and 10 mL)
13) Pipette tips (1 mL, 5 mL, and 10 mL)

[*98] Classified as Class 1 Hazardous Materials (Oxidizing Solids) under the Fire Service Act. Avoid contact with strong acids; store away from combustible materials; and prevent heating, impact, or friction.

(3) Reagents

1) Sulfuric acid[*99,*100,*101] (~95%; specific gravity: ~1.84)
2) Sodium hydroxide solution (10 w/v%)
3) Sodium sulfite solution (10 w/v%)
4) Sodium nitrate[*102]
5) Potassium nitrate[*102]
6) Potassium dichromate[*103]
7) Glacial acetic acid[*100,*101,*104]
8) Acetic acid buffer solution
9) Phosphonic acid solution (50 w/v%)
10) Iodine standard solution (5 $\mu$gI/mL)
11) Pure water (purified by ion exchange or similar processes)
12) Nitrogen gas (purity ≥ 99.99%)

(4) Operation

1) Weigh 0.5 g of the sample and transfer to a 300 mL distillation flask.
2) Add 5 g of potassium dichromate[*105] and 20 mL of pure water, then stir thoroughly.
3) Using a Komagome pipette, gradually add 30 mL of sulfuric acid and stir thoroughly.
4) Heat the mixture on a hot plate at approximately 200°C while occasionally shaking the flask until excess potassium dichromate turns from red to green due to chromium reduction. Rinse the inner surface of the flask with a small amount of sulfuric acid.
5) Add 20 mL of pure water, 0.2 g of sodium nitrate, and 5 mL of the phosphonic acid solution (50 w/v%) in the flask and place it in the distillation apparatus (Figure I.4.1). Place a test tube containing 10 mL of the sodium hydroxide solution (10 w/v%) in the position shown in Figure I.4.1 (center ⑤).
6) Supply nitrogen gas at a rate of 50 mL/min and heat the sample using a mantle heater.
7) Gradually increase the distillation temperature to generate nitrogen dioxide at 120°C. Distill

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[*99] Class III substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*100] Substances subject to hazardous substance labeling under the Industrial Safety and Health Act (those posing potential risks or health hazards to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*101] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

[*102] Classified as Class 1 Hazardous Materials (Oxidizing Solids) under the Fire Service Act. Avoid contact with strong acids; store away from combustible materials; and prevent heating, impact, or friction.

[*103] Class II substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

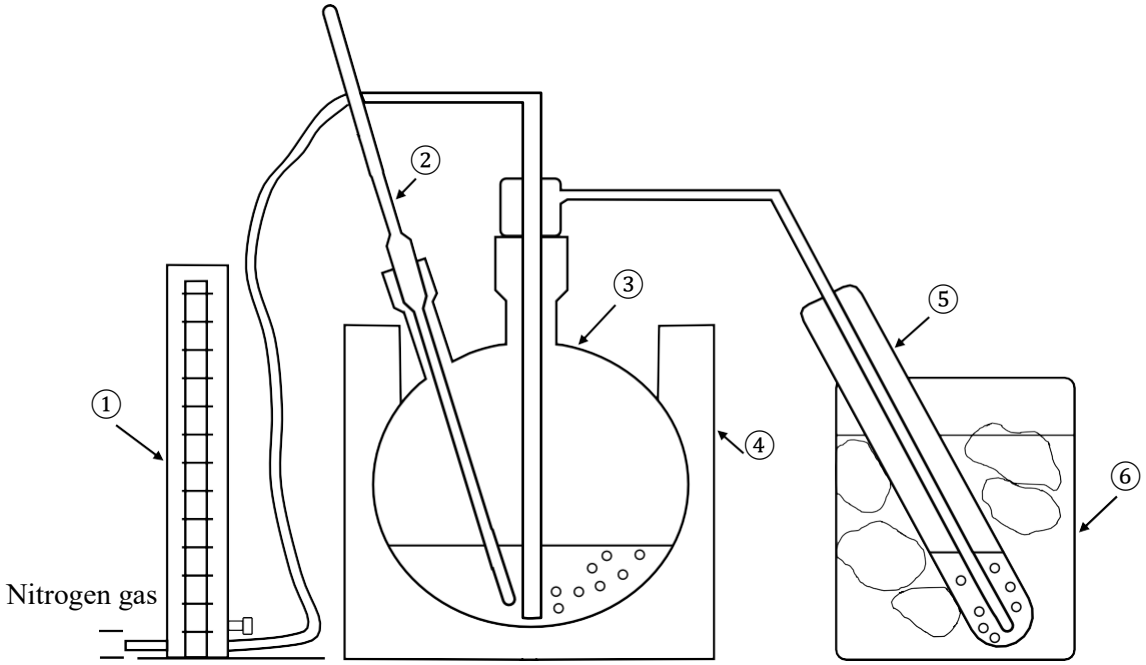
[*104] Classified as a Class IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Following precautions are necessary: open flames must be strictly avoided; store and handle the material below its flash point; ensure that the material is stored separately from Class I and Class V hazardous substances; implement measures to prevent static electricity; when transferring the material to small containers, avoid filling the containers to the full capacity to prevent their rupture due to thermal expansion.

[*105] It decomposes organic matter while oxidizing iodine to $IO_3^-$.

until the brown color of nitrogen dioxide disappears.

8) Remove the distillation tube from the flask and rinse it with pure water. Adjust the washing solution to match the distillate.
9) Transfer the distillate from the test tube to a 100 mL beaker after washing it with pure water.
10) Add 10 mL of the acetic acid buffer solution and 3 mL of the sodium sulfite solution[*106] (10 w/v%).
11) Using glacial acetic acid and the sodium hydroxide solution (10 w/v%), adjust the pH to 5.0[*107], transfer the resulting solution to a 100 mL volumetric flask, and dilute it with pure water so that the volume is 100 mL.
12) Transfer this solution to the 100 mL beaker mentioned in Step 9 and place a rotor inside the beaker.
13) Measure the electrode potential of the ion meter while stirring using a magnetic stirrer.
14) To prepare the calibration curve, collect 0, 1, 5, 10, 15, and 20 mL aliquots from the iodine standard solution (5 $\mu$gI/mL) and place each into a 100 mL beaker. Add purified water to each beaker so that the final volume is ~50 mL. Perform Steps 10–13. A calibration curve is generated newly each time a sample is measured.
15) Determine the amount of iodine in the sample from the calibration curve.

[*106] Reduce $IO_3^-$ to $I^-$.
[*107] Verify using a pH meter.




① Gas flowmeter

② Thermometer (for 200°C)

③ Flask (300 mL)

④ Mantle heater (100 V; 300 W)

⑤ Test tube (30 mL): NaOH solution (10 w/v%; 10 mL)

⑥ Ice water (for cooling)

Figure I.4.1 Distillation apparatus

# Chapter 5 Vegetables, Polished Rice, and Seaweed

Predried samples of vegetables, polished rice, and seaweed are separated and purified using either the activated-carbon adsorption method, wherein iodine is adsorbed onto activated carbon during combustion, or the alkali-solution absorption method, wherein iodine is absorbed by an alkali solution.

Note that the amount of $^{127}I$ contained in vegetables and polished rice[*108,*109] is small. Since 20 mg of iodine carrier is added before analysis, its impact on the recovery rate of iodine from the sample is less than ~0.5%. Therefore, $^{127}I$ in the sample is not quantified.

Although the level of $^{127}I$ in seaweed depends on the sample type, it often contains high levels of $^{127}I$[*110]. Therefore, $^{127}I$ in such samples is quantified as per "5.4 Determination of $^{127}I$ in Seaweed Samples" and subsequently used for recovery rate correction.

## 5.1 Preparation of Reagents

The following text describes the preparation methods for reagents used in the radiochemical analysis of vegetables, polished rice, and seaweed. Reagents should be of the JIS Special Grade. Unless otherwise specified, commercially available products should be used as is. "Pure water" mentioned here refers to water purified by ion exchange or similar processes.

(1) Bases

1) Sodium hydroxide solution (24 w/v%): Dissolve 24 g of sodium hydroxide[*111,*112] in 100 mL of pure water.

[*108] The amount of $^{127}I$ contained in 300 g of vegetables (raw weight equivalent) is at most ~0.1 mg. The approximate $^{127}I$ concentrations in various vegetables are shown below.

| Vegetable | $^{127}I$ concentration (mg/kg wet weight) |
|---|---|
| Cabbage | 0.002 ～ 0.03 |
| Daikon radish | 0.005 ～ 0.01 |
| Onion | 0.003 ～ 0.04 |
| Carrot | 0.003 ～ 0.03 |
| Chinese cabbage | 0.01 ～ 0.02 |
| Spinach | 0.01 ～ 0.1 |

[*109] The amount of $^{127}I$ contained in 50 g of polished rice is at most ~0.005 mg.

[*110] The approximate iodine concentrations and dry residues of various seaweeds are shown below.

| Seaweed | $^{127}I$ concentration (mg/kg wet weight) | Dry residue (%) |
|---|---|---|
| Asakusa Nori (Ama Nori) | 1 ～ 30 | 5 |
| Kombu | 30 ～ 1,300 | 20 |
| Hijiki | 30 ～ 530 | 20 |
| Wakame | 10 ～ 130 | 5 |

[*111] Substances subject to hazardous substance labeling under the Industrial Safety and Health Act (those posing potential risks or health hazards to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*112] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

2) Potassium hydroxide solution (5 w/v%): Dissolve 5 g of potassium hydroxide[*111,*112] in 100 mL of pure water.

(2) Other solutions

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*112,*113] in 100 mL of pure water.
2) Potassium nitrite solution (10 w/v%): Dissolve 10 g of potassium nitrite[*112,*113] in 100 mL of pure water.
3) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of pure water.
4) Potassium sulfite solution (10 w/v%): Dissolve 10 g of potassium sulfite in 100 mL of pure water.
5) Palladium chloride solution (10 mgPd/mL): Add 1.7 g of palladium chloride to 50 mL of pure water and 5 mL of 36% hydrochloric acid[*111,*112,*114], followed by heating. Allow this mixture to cool and then filter it (using the No. 5C filter paper). Then, add pure water to the filtrate so that the final volume is 100 mL. (Refer to Figure I.1.1 while performing the operation.)
6) Iodine carrier solution (20 mgI/mL): Dry approximately 14 g of sodium iodide[*111] at 110°C for 3 hours. Then, cool it for 1 hour in a desiccator. Weigh 11.812 g and dissolve in 50 mL of pure water. Transfer the resulting solution to a brown 500 mL volumetric flask containing 0.2 mL of the sodium hydroxide solution (24 w/v%) and 1 mL of the sodium sulfite solution (10 w/v%). Then, add pure water up to the mark on the volumetric flask Store in a cool, dark place.

[*113] Classified as Class 1 Hazardous Materials (Oxidizing Solids) under the Fire Service Act. Avoid contact with strong acids; store away from combustible materials; and prevent heating, impact, or friction.

[*114] Class III substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

## 5.2 Combustion–Activated Carbon Adsorption Method

### 5.2.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Three-chamber tubular electric furnace (Figure I.1.2)
2) Dryer
3) Balance (weighing range: 0–200 g; readability ≤0.1 mg)

(2) Instruments

1) Quartz tube (Figure I.1.3)
2) Silicone stopper
3) Quartz wool
4) Beaker (100 mL)
5) Watch glass (for 100 mL beakers)
6) Erlenmeyer flask (50 mL)
7) Air cooling tube (approximately 30 cm in length; to be attached to the 50 mL Erlenmeyer flask)
8) Separatory funnel (100 mL)
9) 1-L pressure bottle
10) Separable filter holder (for 20 mm diameter and 42 mm diameter filters)
11) Aspirator
12) Glass funnel (for a 90 mm diameter filter paper)
13) Filter paper
    - Glass-fiber filter paper (47 mm diameter)
    - Separatory filter paper (90 mm diameter)
    - No. 5C filter paper (24 mm diameter)
14) Mounting apparatus
    - Mounting disk (Figure I.1.4)
    - Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/$m^2$)
    - Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
    - Stainless steel sample dish (25 mm diameter)
    - Holding device (Figure I.1.5)
15) Micropipette (1 mL and 5 mL)
16) Pipette tips (1 mL and 5 mL)
17) Hand burner (for city gas or propane gas)
18) Desiccator
19) Hot plate

(3) Reagents

1) Nitric acid[*115,*116,*117] (mass fraction: 60%–61% (approximately 13 mol/L); density: 1.38 g/mL)
2) Sodium hydroxide solution (24 w/v%)
3) Sodium nitrite solution (10 w/v%)
4) Sodium sulfite solution (10 w/v%)
5) Palladium chloride solution (10 mgPd/mL)
6) Iodine carrier solution (20 mgI/mL)
7) Xylene[*116,*117,*118,*119]
8) Pure water (purified by ion exchange or similar processes)
9) Activated carbon
10) Copper oxide[*116] (needle-shaped)
11) Gases
    - Oxygen gas (purity ≥ 99.999%)
    - Nitrogen gas (purity ≥ 99.99%)
    - City gas or propane gas

### 5.2.2 Analytical Operations

(1) Pretreatment of various samples

① Vegetables[*120]

1) Dry approximately 1 kg of the sample at ~70°C. After pulverizing, weigh approximately 30 g of the sample and place it in the inner tube of a quartz tube (Figure I.1.2). When doing so, prepack the narrower end of the inner tube with quartz wool.
2) Add 1 mL of the iodine carrier solution (20 mgI/mL) and seal the end with quartz wool[*121].

[*115] Class III substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*116] Substances subject to hazardous substance labeling under the Industrial Safety and Health Act (those posing potential risks or health hazards to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*117] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

[*118] Class II substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*119] Guidelines for Prevention of Health Hazards from Chemical Substances Designated by the Ministry of Health, Labour and Welfare in accordance with Article 28, Paragraph 3 of the Industrial Safety and Health Act apply. Measures must be undertaken to reduce exposure to target substances.

[*120] The apparatus illustrated in Figure I.1.3 can burn ~30 g of sample at a time.

[*121] During combustion, components within the sample may form gases, causing the pressure within the quartz tube to increase. Therefore, extreme caution is necessary.

② Polished rice

1) Weigh ~50 g of the pulverized polished rice sample and place it in the inner tube of a quartz tube (Figure I.1.2)[*122]. When doing so, prepack the narrower end of the inner tube with quartz wool.
2) Add 1 mL of iodine carrier solution (20 mgI/mL) and seal the end with quartz wool.

③ Seaweed[*123]

1) Dry ~1 kg of the sample at ~70°C and then weigh it. Prior to drying, determine the amount of $^{127}$I in the sample as per "5.4 Determination of $^{127}$I in Seaweed Samples"[*124]. Determine the test sample amount based on the identified amount of $^{127}$I in the sample. Place the sample in the inner tube of the quartz tube (Figure I.1.2) prepacked with quartz wool at the narrow end.
2) For samples containing ≤20 mg of iodine, add the iodine carrier solution (20 mgI/mL) to adjust the iodine content in the specimen to ~20 mg. Then, seal the ends with quartz wool[*125].

(2) Combustion of samples

Perform the same operation as in "(2) Combustion of samples" in "1.2 Combustion–Activated Carbon Adsorption Method" described in "Chapter 1 Airborne Particulate Matter Samples."

(3) Chemical separation of iodine after combustion

Perform the same operation as in "(3) Chemical separation of iodine after combustion" in "1.2 Combustion–Activated Carbon Adsorption Method" described in "Chapter 1 Airborne Particulate Matter Samples."

## 5.3 Combustion–Alkali Solution Absorption Method

### 5.3.1 Equipment, Instruments, and Reagents

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

(1) Equipment

1) Double-chamber tubular electric furnace (Figure I.1.8)
2) Dryer
3) Balance (weighing range: 0–200: g; readability ≤0.1 mg)

(2) Instruments

1) Quartz tube (Figure I.1.2)
2) Silicone stopper
3) Quartz wool
4) Gauze

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[*122] When placing polished rice in the inner tube, it is advisable to leave sufficient space at the top of the inner tube as rice may expand during heating.

[*123] Depending on the sample shape, up to ~30 g of sample can be burned at a time.

[*124] If the amount of $^{127}$I exceeds 50 mg, a sample with $^{127}$I amount exceeding 50 mg must be prepared for generating the counting efficiency curve during "6.1.2 Preparation of Samples for Generating Counting Efficiency Curves" described in "Chapter 6 Measurement."

[*125] Iodine may remain in the combustion residue, potentially reducing the iodine recovery rate.

5) Beakers (100 mL and 500 mL)
6) Watch glass (for 100 mL beakers)
7) Gas washing bottle (200 mL)
8) Separatory funnel (100 mL)
9) 1 L pressure bottle
10) Separable filter holder (for 20 mm diameter filters)
11) Aspirator
12) Glass funnel (for a 90 mm diameter filter paper)
13) Filter paper
    - Glass-fiber filter paper (90 mm diameter)
    - Separatory filter paper (90 mm diameter)
    - No. 5C filter paper (24 mm diameter)
14) Mounting apparatus
    - Mounting disk (Figure I.1.4)
    - Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/m$^2$)
    - Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
    - Stainless steel sample dish (25 mm diameter)
    - Holding device (Figure I.1.5)
15) Micropipette (1 mL and 5 mL)
16) Pipette tips (1 mL and 5 mL)
17) Desiccator
18) Hot plate

(3) Reagent
1) Nitric acid[*126,*127,*128] (mass fraction: 60–61% (~13 mol/L); density: 1.38 g/mL)
2) Potassium hydroxide[*127,*128]
    - Potassium hydroxide (granules)
    - Potassium hydroxide solution (5 w/v%)
3) Potassium sulfite
    - Potassium sulfite (granules)
    - Potassium sulfite solution (10 w/v%)
4) Potassium sulfite solution (10 w/v%)
5) Palladium chloride solution (10 mgPd/mL)
6) Iodine carrier solution (20 mgI/mL)

[*126] Class III substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.
[*127] Substances subject to hazardous substance labeling under the Industrial Safety and Health Act (those posing potential risks or health hazards to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.
[*128] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

7) Xylene[*127,*128,*129,*130]
8) Pure water (purified by ion exchange or similar processes)
9) Activated carbon
10) Copper oxide[*127] (needle-shaped)
11) Gases
    ・Oxygen gas (purity ≥ 99.999%)
    ・Nitrogen gas (purity ≥ 99.99%)

### 5.3.2 Analytical Operations

(1) Pretreatment of various samples

Perform the same operations as in "(1) Pretreatment of various samples" in "5.2 Combustion–Activated Carbon Adsorption Method."

(2) Combustion of samples

Perform the same operations as those described in "(2) Combustion of samples" in "1.3 Combustion–Alkali Solution Absorption Method" described in "Chapter 1 Airborne Particulate Matter Samples."

(3) Chemical separation of iodine after combustion

Perform the same operation as in "(3) Chemical separation of iodine after combustion" in "1.3 Combustion–Alkali Solution Absorption Method" described in "Chapter 1 Airborne Particulate Matter Samples."

## 5.4 Determination of $^{127}$I in Seaweed Samples

The procedure is same as "4.4 Determination of $^{127}$I in Soil Samples" described in "Chapter 4 Soil."

[*129] Class II substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Class I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, must be implemented.

[*130] Guidelines for preventing health hazards caused by chemical substances, established by the Ministry of Health, Labour and Welfare in accordance with the provisions of Article 28, Paragraph 3 of the Industrial Safety and Health Act, apply. Measures must be undertaken to reduce exposure to target substances.

# Chapter 6 Measurement

Measure γ-rays (39.578 keV) or β-rays (189.3 keV) emitted by $^{129}$I in the measurement samples prepared as per methods described in Chapters 1–5[*131].

## 6.1 Counting Efficiency Curve

Using the iodine carrier solutions and the $^{129}$I standard solutions, prepare several palladium iodide precipitates of different weights and use them as samples for generating counting efficiency curves during γ-ray or β-ray measurements.

### 6.1.1 Preparation of Reagents

The following text describes the preparation methods for reagents used in preparing samples for generating counting efficiency curves. The reagents should be of the JIS Special Grade. Unless otherwise specified, commercially available products should be used as is. "Pure water" used here refers to water purified by ion exchange or similar processes.

(1) Radioactive standard solution[*132]

1) $^{129}$I standard solution: Prepare this solution using a commercially available product by following the procedure described in "(4) Preparation of the $^{129}$I standard solution" below to achieve the specified concentration.

(2) Bases

1) Lithium hydroxide solution (0.1 w/v%): Dissolve 0.175 g of lithium hydroxide monohydrate[*133,*134] in 100 mL of pure water.

(3) Other solutions

1) Sodium sulfite

- Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of pure water.

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[*131] For the decay diagrams of $^{129}$I, refer to "Common Appendix A Nuclear Data and Decay Diagram for $^{129}$I."

[*132] The Act on the Regulation of Radioactive Isotopes and Related Substances applies. These substances require permission and notification for use, notification for sale or rental activities, and permission for disposal-related business activities. The Nuclear Regulation Authority Notification No. 6 of March 18, 2020, titled "To Determine the Quantity, etc. of Radioactive Isotopes," specifies the lower limit quantities (notified quantities) for each nuclide. The ratio "Bq held/notified Bq" should be calculated for all nuclides held by a facility in use, and the sum of these ratios should not exceed "1." In addition, the June 2005 Enforcement Order of the Act on the Regulation of Radioactive Isotopes and Related Substances introduced lower limit quantities for each nuclide. When the amount of a radionuclide handled remains below the associated limit, its use outside of a controlled area is permitted. During practical use, refer to the "Safety Manual for the Use of Non-Sealed Radioisotopes Below the Lower Limit Quantity" published by the Japan Isotope Association (https://www.jrias.or.jp/report/cat1/308.html).

[*133] Substances subject to hazardous substance labeling under the Industrial Safety and Health Act (those posing potential risks or health hazards to workers): Labeling, provision of safety data sheets, and risk assessment (including risk-reduction measures) are mandatory. In addition, workers must receive information and training regarding these requirements.

[*134] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

- Sodium sulfite solution (0.1 w/v%): Dissolve 0.1 g of sodium sulfite in 100 mL of pure water.

2) Sodium iodide solution (0.01 w/v%): Dissolve 0.01 g of sodium iodide[*133] in 100 mL of pure water. Prepare in brown glassware and store in a cool, dark place.
3) Palladium chloride solution (10 mgPd/mL): Add 1.7 g of palladium chloride to 50 mL of pure water and 5 mL of hydrochloric acid, followed by heating. Allow the mixture to cool and filter it (using the No. 5C filter paper). Add pure water to the filtrate so that the final volume is 100 mL. (Refer to Figure I.1.1 while performing the operation).
4) Iodine solution

- Iodine carrier solution (20 mgI/mL): Dry ~14 g of sodium iodide at 110°C for 3 hours. Then, allow it to cool for 1 hour in a desiccator. Weigh 11.812 g and dissolve in 50 mL of pure water. Transfer the resulting solution in a brown 500 mL volumetric flask containing 0.2 mL of the sodium hydroxide solution (24 w/v%) and 1 mL of the sodium sulfite solution (10 w/v%). Then, add pure water up to the mark on the volumetric flask Store in a cool, dark place.
- Iodine carrier solution (5 mgI/mL): Dilute the iodine carrier stock solution (20 mgI/mL) 4-fold with pure water immediately before use.

(4) Preparation of the $^{129}$I standard solution

The following steps describe the preparation procedure for a standard solution of $^{129}$I with a concentration of ~0.04 kBq/g. Calculate the amount and concentration of the solution to be used appropriately based on the actual concentration of the obtained standard solution.

1) Wash and dry a 250 mL brown volumetric flask.
2) Weigh the dried volumetric flask on an analytical balance to determine its tare weight.
3) Add 2.5 mL of the sodium sulfite solution (0.1 w/v%) to the tare-measured volumetric flask.
4) Add 2.5 mL of the lithium hydroxide solution (0.1 w/v%) to the flask.
5) Add 2.5 mL of the sodium iodide solution (0.01 w/v%) to the flask.
6) Add ~150 mL of pure water to the flask.
7) Weigh a 20 mL capped sample bottle to 0.01 mg to determine its tare weight.
8) Add an aliquot (~6.25 g) of the $^{129}$I standard solution in the sample bottle, seal it, and then measure its weight. Subtract the tare weight of the sample bottle from its total weight to determine the aliquoted amount (g) of the $^{129}$I standard solution. Calculate the activity (Bq) of added $^{129}$I based on the concentration (kBq/g) of the $^{129}$I standard solution.
9) Transfer the aliquoted $^{129}$I standard solution to the volumetric flask prepared in Step 6. Rinse the sample bottle with pure water and transfer the rinse solution to the volumetric flask.
10) Add pure water to the volumetric flask mentioned in Step 9 up to the mark. Weigh the flask, subtract the tare weight of the measuring flask from that weight, and record the result as the weight of the prepared solution.
11) After mixing well, store in a cool, dark place.

In some cases, aliquot into brown 50 mL ampoule tubes, place the tubes in a polyethylene bag,

and store them by sealing the bag using a vacuum sealer to remove air.

### 6.1.2 Preparation of Samples for Generating Counting Efficiency Curves

(1) Equipment

1) Low-energy photon spectrometers (LEPSs) or n-type germanium semiconductor detectors (both required for γ-ray measurements)
2) Low-background gas flow counter (hereinafter referred to as "LBC"; required for β-ray measurements)

(2) Instruments

1) Beaker (100 mL)
2) Separable filter holder (for 20 mm diameter filters)
3) Mounting apparatus
   - Mounting disk (Figure I.1.4)
   - Polyethylene terephthalate (PET) film (Figure I.1.4; ≤0.8 mg/m$^2$)
   - Ring (Figure I.1.4; outer diameter: 24 mm; inner diameter: 21.8–21.9 mm)
   - Stainless steel sample dish (25 mm diameter)
   - Holding device (Figure I.1.5)
4) Micropipettes (1 mL, 2 mL, 5 mL, and 10 mL)
5) Pipette tips (1 mL, 2 mL, 5 mL, and 10 mL)
6) Desiccator

(3) Reagent

1) $^{129}$I standard solution ($^{129}$I: 10 Bq/mL)
2) Sodium sulfite solution (10 w/v%)
3) Palladium chloride solution (10 mgPd/mL)
4) Iodine carrier solution (5 mgI/mL)

(4) Operation

1) Aliquot 5 mL of the $^{129}$I standard solution ($^{129}$I: 10 Bq/mL) into five 100 mL beakers.
2) Add 2, 4, 6, 8, and 10 mL of the iodine carrier solution (5 mgI/mL) to each of these beakers.
3) Add water to each beaker so that the total volume is 20 mL. Then, add 0.5 mL of the sodium sulfite solution (10 w/v%) and stir. Add 3 mL of the palladium chloride solution (10 mgPd/mL) to produce a precipitate of palladium iodide. (Refer to Figure I.1.6 while performing the operation).
4) Heat the solution on a hot plate until boiling. After cooling, suction-filter the precipitate (using a filter paper of known weight (No. 5C; 25 mm diameter), the separable filter holder, and a pressure bottle). Discard the filtrate.
5) Dry the precipitate together with the filter paper in a dryer at 80°C for 1 hour. Then, allow it to cool for 30 minutes in a desiccator.

6) Weigh the sediment and calculate the recovery rate.
7) Place the precipitate with the filter paper onto the mounting disk, cover with a PET film, and secure it with a ring. Trim the film protruding from the ring, transfer it to a sample dish, and use it as a sample for generating a counting efficiency curve. (Refer to Figures I.1.5 and I.1.7 while performing the operation).

## 6.2 Gamma Ray Spectrometry

LEPSs or n-type germanium semiconductor detectors[*135], together with broadband (≥10 keV) X-ray and γ-ray NaI(Tl) scintillation detectors, are used to measure γ-rays emitted by $^{129}$I (energy: 39.578 keV)[*136] and quantify $^{129}$I in the sample.

### 6.2.1 Measurement Method

Analyze the samples used for generating the counting efficiency curve for ~80,000 seconds using an LEPS or n-type germanium semiconductor detector set to operate at ~0.2 keV/ch. Place the sample such that the precipitate faces the detector surface and is as close to the detector as possible.

### 6.2.2 Calculation of Radioactivity Concentration

(1) In the obtained spectrum, set the peak region and baseline region for the target γ-ray (39.57 keV) and determine the peak area. The peak and baseline regions for the sample should be set to the same channels as those used for creating the counting efficiency curve. However, if other peaks are observed in the baseline region, avoid those areas and adjust the baseline region accordingly[*137].

(2) Generate a counting efficiency curve from the measurement results.

1) Determine the counting efficiency for each sample according to the following equation:

$$\varepsilon = \frac{N_s \times 100}{t \times B \times Y}$$

$$Y = \frac{W_p \times R}{W_1} \times 100$$

$\varepsilon$ : $^{129}$I counting efficiency (cps/Bq)
$t$ : Measurement time (s)
$B$ : activity of added $^{129}$I (Bq)
$Y$ : Recovery rate (%)
$Ns$ : Net count value at peak
$W1$ : Amount of $^{127}$I added as a carrier (mg)

[*135] Unlike conventional p-type germanium semiconductor detectors, LEPSs or n-type germanium semiconductor detectors can measure energies exceeding ~10 keV due to their thin incident windows.
[*136] Some broadband NaI scintillation survey meters have been reported to measure X-rays in the 10–200 keV energy range with high sensitivity. In addition, they can measure ambient dose equivalents of up to 4 μSv/h. (S.Yamamura et al.: Development of Wide-energy Range X/γ-ray Survey-meter, Journal of Nuclear Science and Technology, Supplement 5, 187-190 (2008))
[*137] For details, refer to The Series of Environmental Radioactivity Measuring Methods No. 7 "Gamma-ray Spectrometry Using a Germanium Semiconductor Detector."

$Wp$ : Weight of the palladium iodide precipitate (mg)

$R$ : Weight ratio of $^{127}$I in palladium iodide (0.7046)

2) Plot the counting efficiency curve with counting efficiency ($\varepsilon$) on the vertical axis and the $^{127}$I carrier amount (mg) on the horizontal axis. Figure I.6.1 shows an example of a counting efficiency curve obtained using a LEPS.

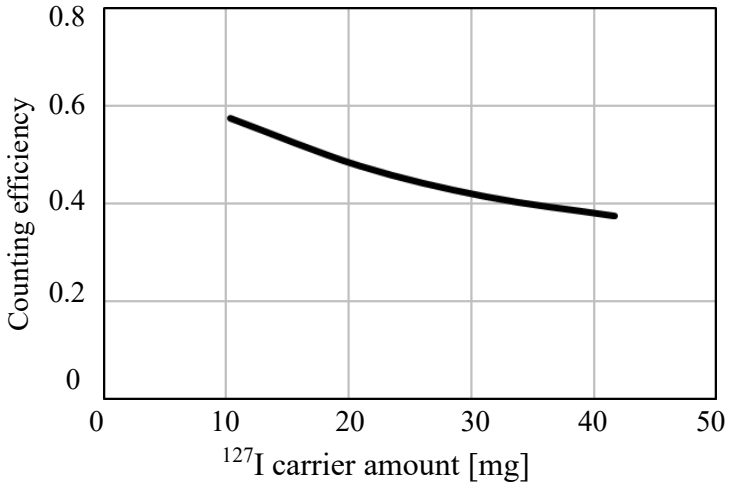



Figure I.6.1 Example of a counting efficiency curve
(obtained using a LEPS)

(3) The radioactivity concentration of $^{129}$I in the sample and its counting error are determined according to the following equations:

$$A = \frac{N_n \times 100}{t_s \times \varepsilon \times Y \times W_s}$$

$$\sigma_A = \frac{\sigma_{N_n} \times 100}{t_s \times \varepsilon \times Y \times W_s}$$

$$N_n = N_s - N_0$$

$$\sigma_{N_n} = \sqrt{N_s + N_0}$$

$$Y = \frac{W_p \times R}{W_1 + C_I \times W_s} \times 100$$

$A$ : Radioactivity concentration of $^{129}$I in the sample (in Bq/kg, Bq/L, etc.)

$t_s$ : Sample measurement time (s)

$\varepsilon$ : $^{129}$I counting efficiency (cps/Bq) (corresponding to the amount of iodine present in the sample; determined from the counting efficiency curve)

$Y$ : Recovery rate (%)

$W_s$ : Sample quantity (kg, L, etc.)

$N_n$ : Net count value at peak of the sample

$\sigma_A$ : Error in the radioactivity concentration $A$ of $^{129}$I in the sample (Bq/kg, Bq/L, etc.)

$\sigma_{Nn}$ : Counting error of the net count value at peak of the sample

$N_s$ : Count values in the sample peak region

$N_0$ : Count value in the baseline region of the sample

$W_1$ : Amount of $^{127}$I added as a carrier (mg)
$C_I$ : Concentration of $^{127}$I in the sample (mg/kg, mg/L, etc.)
$W_p$ : Weight of precipitated palladium iodide (mg)
$R$ : Weight ratio of $^{127}$I in palladium iodide (0.7046)

## 6.3 Measurement of β-rays Using an LBC

β-rays (189.3 keV) emitted by $^{129}$I are measured using an LBC[*138] to quantify the concentration of $^{129}$I in the sample.

### 6.3.1 Measurement Method

Alternately measure the sample used for generating the counting efficiency curve and the background for ~100 minutes. The prepared measurement sample, which is precipitated as palladium iodide, is measured for ~100 minutes, alternating between the sample and background[*139].

### 6.3.2 Calculation of Radioactivity Concentration

(1) The net counting rate and its counting error should be determined according to the following equations:

$$r_n = \frac{N_s}{t_s} - \frac{N_0}{t_0}$$

$$\sigma_{r_n} = \sqrt{\frac{N}{t^2} + \frac{N_0}{{t_0}^2}}$$

$r_n$ : $^{129}$I net counting rate
$t_s$ : Sample measurement time (s)
$N_s$ : Sample count value
$t_0$ : Background measurement time (s)
$N_0$ : Background count value
$\sigma_{rn}$ : Counting error of the $^{129}$I net counting rate

(2) Generate the counting efficiency curve from the measurement results of the calibration samples.

1) Determine the counting efficiency for each sample used to generate counting efficiency curves according to the following equation:

$$\varepsilon = \frac{r_{std} \times 100}{B \times Y}$$

$$Y = \frac{W_p \times R}{W_1} \times 100$$

$\varepsilon$ : $^{129}$I counting efficiency (cps/Bq)
$B$ : activity of added $^{129}$I (Bq)
$Y$ : Recovery rate (%)

[*138] The β-ray energy of $^{129}$I is low (189.3 keV); hence, it is preferable to use a window-less detector.
[*139] To ensure that the measuring instrument is not contaminated, alternate between measuring the sample and the background.

$r_{std}$ : Net counting rate (cps) of $^{129}$I in the sample used for generating the counting efficiency curve

$W_1$ : Amount of $^{127}$I added as a carrier (mg)

$W_p$ : Weight of precipitated palladium iodide (mg)

$R$ : Weight ratio of $^{127}$I in palladium iodide (0.7046)

2) Plot a counting efficiency curve with counting efficiency ($\varepsilon$) on the vertical axis and the $^{127}$I carrier amount (mg) on the horizontal axis. Figure I.6.2 shows an example of a counting efficiency curve obtained using an LBC.

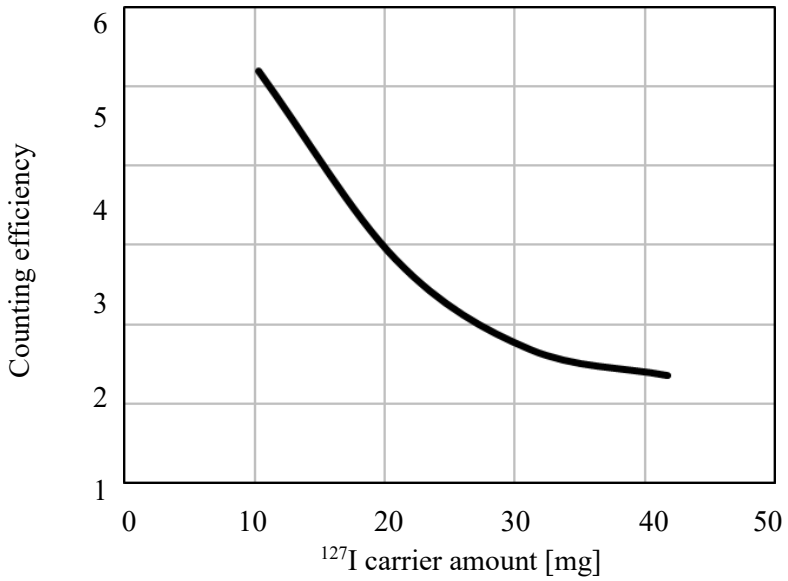



Figure I.6.2 Example of a counting efficiency curve (obtained using an LBC)

(3) The radioactivity concentration of $^{129}$I in the sample and its counting error are determined according to the following equations:

$$A = \frac{r_n \times 100}{\varepsilon \times Y \times W_s}$$

$$\sigma_A = \frac{\sigma_{r_n} \times 100}{\varepsilon \times Y \times W_s}$$

$$Y = \frac{W_p \times R}{W_1 + C_I \times W} \times 100$$

$A$ : Radioactivity concentration of $^{129}$I in the sample (Bq/kg, Bq/L, etc.)

$\varepsilon$ : $^{129}$I counting efficiency (cps/Bq) (corresponding to the amount of iodine in the sample; determined from the counting efficiency curve)

$Y$ : Recovery rate (%)

$W_s$ : Sample quantity (kg, L, etc.)

$r_n$ $^{129}$I Net counting rate (cps)

$\sigma_A$ : Error in the radioactivity concentration $A$ (Bq/kg, Bq/L, etc.)

$\sigma_{rn}$ : Counting error of the $^{129}$I net counting rate

$W_1$ : Amount of $^{127}$I added as a carrier (mg)

$C_I$ : Concentration of $^{127}$I in the sample (mg/kg, mg/L, etc.)

$W_p$ : Weight of precipitated palladium iodide (mg)

$R$ : Weight ratio of $^{127}$I in palladium iodide (0.7046)

## 6.4 Uncertainty

Measurement uncertainty is used as an indicator to assess the reliability of measurement results. Measurement uncertainty is a parameter associated with the measurement result that characterizes the dispersion of values that could reasonably be attributed to the measurand[*140]. Notably, measurement uncertainty is not the variation inherent in individual measurement results. Rather, it is a value indicating the potential variation inherent in a series of measurements.

In the past, it was common practice to determine and report only the statistical uncertainty (counting error) in radioactivity measurements based on the count statistics. In the analysis of low-level environmental samples, although the statistical uncertainty is often dominant, uncertainty also results from other sources throughout the analytical process, including sample preparation and instrument calibration; therefore, it is necessary to evaluate uncertainty at each stage. By evaluating uncertainty, it is possible to determine whether the analytical results of different laboratories agree or disagree in proficiency testing and interlaboratory comparisons. Furthermore, by identifying the steps with the greatest uncertainty and implementing measures to reduce it, it is possible to improve the quality of analytical results.

For details on uncertainty evaluation in the radiochemical analysis of $^{129}$I, refer to Explanation A.

## 6.5 Lower Detection Limit

The lower detection limit in radioactivity measurements varies depending on factors such as the sample quantity, measurement time, and background counting rate. Therefore, the target lower detection limit should be set according to the purpose of the analysis and measurement. The determination of whether a detection is positive or negative is generally made based on whether the net counting rate exceeds three times the statistical uncertainty. Calculating the lower detection limit provides an indication of the lowest radioactivity level that can be reliably detected from the measurements. Environmental radioactivity is often too weak to be detected. Therefore, it is desirable to obtain the lower detection limit when measuring analytical samples. Notably, although radioactivity above the lower detection limit will almost always be detected, radioactivity below this limit is not necessarily undetectable and may still be detected.

Methods for calculating the detection limit include Cooper's method[*141], Kaiser's method[*142,*143], Currie's method[*144], and the evaluation method specified in ISO 11929[*145]. The

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

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

[*142] H.Kaiser: Zum Problem der Nachweisgrenze, Fresenius' Zeitschrift für analytische Chemie, 209, 1-18 (1965)

[*143] 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 and Apply Chemistry, 45, 105-123 (1976)

[*144] L.A. Currie: Limits for qualitative detection and quantitative determination Application to Radiochemistry, Analytical Chemistry, 40, 586-593 (1968)

[*145] 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 application (2022)

appropriate method should be selected in accordance with the study aims/objectives. When reporting the lower detection limit, it is necessary to clearly state the evaluation method used as well as the associated confidence (risk) level.

Furthermore, when considering the concept of each lower detection limit, it is necessary to take into account the distribution of measured values. When a measurement target is measured a sufficient number of times, the resulting values can be represented by a mathematical model known as a normal (Gaussian) distribution, with the mean at the peak, as illustrated in Figure I.6.3.

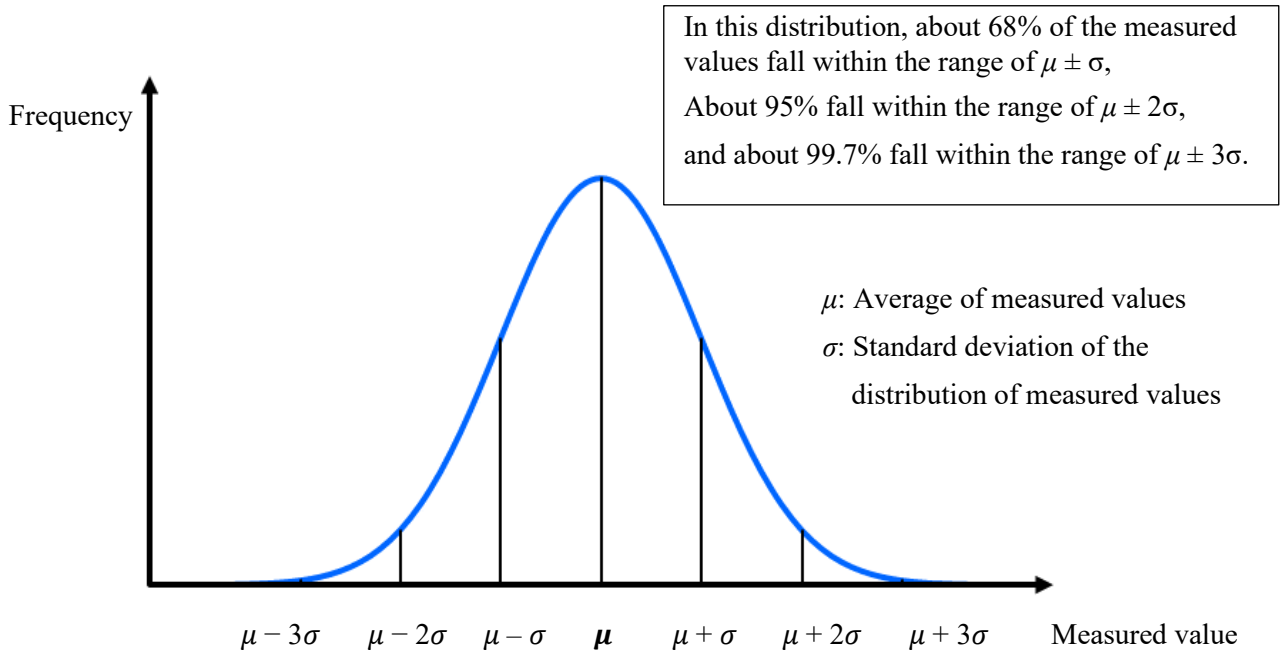



Figure I.6.3 Distribution of measured values

To date, Kaiser's method has been used to derive the detection limit, which can be calculated simply based on the sample measurement time, background measurement time, and background counting rate. For the sake of harmonizing national measurement standards, the general uncertainty of radiation measurements and associated decision thresholds and detection limits have been specified by ISO 11929 and are now being adopted in evaluations. The method for calculating the detection limit of measurement is to be selected by the user. However, the method used for evaluation should be explicitly stated as necessary. Evaluation methods based on ISO 11929 and Kaiser's method are discussed in "Explanation B  Example of Calculating the Lower Detection Limit."

# Chapter 7 Quality Assurance

It is extremely important to conduct routine inspections to ensure traceability, including compliance to national standards, and guarantee the integrity of equipment, in addition to performing analyses and measurements following the procedures described in this document. By continuously implementing these measures, one can demonstrate to third parties that the quality of analysis results is assured. To ensure the quality of analytical results, it is ideal to implement procedures in accordance with the principles of ISO/IEC 17025. These procedures are broadly categorized into internal quality control procedures, performed by analysts and measurement personnel themselves, and external quality control procedures, such as participation in proficiency testing programs conducted by external organizations.

## 7.1 Internal Quality Control

### 7.1.1 Ensuring Traceability

Traceability must be ensured for the following items in the analysis results: radioactivity (Bq) and mass (kg). For the former, traceability must be ensured for measuring instruments calibrated using standard liquid sources. For the latter, traceability must be ensured for electronic balances used during sample preparation. 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. Additionally, for electronic balances, manufacturers offer calibration services. Therefore, performing maintenance inspections that include the issuance of calibration certificates is sufficient. Equipment calibration should be performed at appropriate intervals, and calibration validity periods must be established and managed. Within the validity period, verify that no changes affecting analysis results have occurred in the equipment, as described in "7.1.2 Routine Inspection."

Traceability should also be ensured for records and other documents that accompany analytical results. Specifically, it is important that the collection record sheet—which records the collection date and location of samples, assigns a unique number (e.g., analysis number) to samples, and stores all records and forms generated during analysis and measurement—is managed in a continuous, traceable manner.

### 7.1.2 Routine Inspection

Inspection items and methods pertaining to instruments used in $^{129}$I analysis and measurement are described below. To determine whether the instrument is sound and usable, it is necessary to establish acceptance criteria for all inspection items. It is ideal to establish provisional standards based on experimentally obtained initial data and then modify them into permissible standards[*146] through statistical processing once data has been accumulated. Notably, the objective is to verify

[*146] It is convenient to calculate the mean and standard deviation and then set the tolerance range as $\pm k\sigma$ (where $k$ is either 2 or 3) centered around the mean. Additionally, when performing maintenance and inspection of equipment, consider whether the tolerance standards should be reviewed.

that no changes affecting analytical results have occurred in the equipment; therefore, verification may be conducted using methods other than those discussed here. The dates of daily inspections, persons in charge, and inspection results should be recorded and retained.

If the results of routine inspections indicate that equipment does not meet acceptable criteria, its use must be temporarily suspended. Further, the cause should be investigated, and the issue should be resolved. If the issue cannot be resolved through remeasurement or equipment reconfiguration, inspection or repair by the manufacturer should be carried out.

(1) Measuring instruments

Regularly inspect LEPSs, LBCs, and other equipment to ensure no changes affecting analytical results have occurred in the instruments. Ideally, this inspection should be performed each time measurements are conducted.

・Counting efficiency

By analyzing a standard radioactive source[*147] showing fixed radioactivity under identical conditions and determining whether the obtained count value (or counting rate) falls within the tolerance criteria, we can determine whether there are changes in the counting efficiency significant enough to affect the analytical results. Note that when verifying changes in the counting efficiency, the decay of the radionuclides contained in the standard source must be taken into account.

・Installation environment

Install the measuring equipment in a location with appropriate air conditioning and verify that the installation environment is stable.

Furthermore, it is advisable to have the manufacturer perform periodic inspection approximately once every one or two years. At that time, e.g., for an LBC, it is advisable to have the manufacturer verify not only the plateau and efficiency characteristics but also the power supply, input sensitivity, and elevator and turntable operations.

(2) Electronic balance

Regularly inspect the electronic balance to ensure no changes affecting analytical results have occurred in the instrument. It is recommended to perform inspections each time before the equipment is used and conduct regular inspections on a monthly basis or a similar schedule.

・Preuse inspection

This is inspection performed before using the balance. For balances equipped with built-in weights, it is recommended to perform internal calibration prior to use. Conduct a preuse inspection of the electronic balance using a weight close to the mass of the actual sample to be weighed (or the lower limit of the usage range)[*148] and confirm whether the weighing

[*147] The source and the actual measuring container used need not to be of the same shape.
[*148] Calibration-certified weights (OIML (JIS) Class F2 or higher) are preferred.

result is within the tolerance standard[*149]. It is advisable to perform the same inspection again after use.

・Periodic inspections

Verify the sensitivity of the electronic balance using a weight close to the maximum capacity of the device. For balances equipped with built-in weights, it is recommended to perform internal calibration prior to use. The grade and tolerance criteria for weights used can follow those established for preuse inspections. Periodic inspections should ideally be conducted at intervals of approximately one month.

Balances should ideally undergo periodic inspections by the manufacturer or an equivalent qualified party approximately once per year.

(3) Micropipette

Regularly inspect the micropipette to confirm that no changes have occurred that can affect analytical results. Ideally, preuse inspection should be conducted each time a carrier solution is added.

・Preuse inspection

This is inspection performed prior to adding the iodine carrier solution. Using a micropipette, aliquot 1 mL of pure water and weigh it using an electronic balance. Ensure that the final weight is 1 g. Verify that the weighing results fall within the tolerance limits specified in the calibration certificate for the micropipette.

Micropipettes should also undergo periodic inspections by the manufacturer or an equivalent party approximately once a year.

(4) Management of reagents and reference materials

Use reagents, standards, and other items with a stated warranty period within that period. Moreover, for items without such labeling, manage the opening date and other details to ensure quality control of reagents and other materials.

## 7.2 External Quality Control

### 7.2.1 Interlaboratory Comparison

By conducting interlaboratory comparisons using the same sample (preferably with ISO/IEC 17025 accredited laboratories) and confirming that no significant differences exist between the analytical results, the validity of the measurement and analysis processes can be verified.

[*149] The tolerance standard must be determined based on weighing uncertainty, minimum weighing value, and safety factor; however, an initial value of 0.5% may be set as the control range. (Example: For a 10-g weight, the tolerance range will be 9.95–10.05 g).

### 7.2.2 Technical Proficiency Test

Participation in proficiency tests conducted by external organizations (preferably those accredited to ISO/IEC 17043) allows laboratories to objectively demonstrate their proficiency by comparing the analytical results of test specimens with actual results. For proficiency tests based on ISO/IEC 17043, metrics such as Z-scores and En-scores are used to evaluate the performance of participating laboratories.

# Explanation

## Explanation A : Example of Uncertainty Evaluation

Regarding how to evaluate and express the reliability of measurement results, several differing approaches have traditionally existed across countries and technical fields, causing confusion. Therefore, the International Committee for Weights and Measures (CIPM) raised this issue in the late 1970s. This led to several international organizations involved in measurement working together to establish a unified method for evaluating and expressing the reliability of measurement results. The result of this effort was the "Guide to the Expression of Uncertainty in Measurement" (hereinafter referred to as the "GUM") published in 1993 under the joint authorship of seven international organizations, including International Organization for Standardization (ISO). The GUM is based on the understanding that quantities such as "true value" or "error," which are fundamentally unknowable, should not be incorporated into the evaluation procedure. To distinguish it from conventional concepts of a similar kind, "uncertainty" was introduced as a new indicator of measurement reliability, representing the variability of measurements. The uncertainty evaluation approach described in the GUM has been recognized for its high technical rationality and consistency. Consequently, "uncertainty" has rapidly gained widespread adoption and is now extensively used in various contexts where expressing the reliability of measurements is critical.

In environmental radiation monitoring, measurement results obtained are increasingly referenced domestically and internationally, making it increasingly necessary for them to be traceable to appropriate measurement standards. Establishing internationally agreed-upon measurement traceability requires several essential elements, such as an unbroken chain of calibration. The evaluation of measurement uncertainty is one of these elements, and result calculation and presentation must be carried out according to agreed-upon methods, specifically those based on the GUM. Furthermore, in proficiency tests conducted by International Atomic Energy Agency (IAEA), participating analytical laboratories are required to report measurement results, including uncertainty. Thus, by employing "uncertainty" as an indicator of reliability for internationally recognized measurement results, the international consistency, reliability, and equivalence of results are ensured. Furthermore, to demonstrate with high confidence that the radioactivity concentration in environmental samples does not exceed the reference value, the upper limit considering uncertainty is sometimes compared with the reference value.

In this way, the evaluation of measurement uncertainty has become widely recognized as a standard method for objectively demonstrating the reliability of environmental radiation monitoring results. Domestic analytical institutions are encouraged to adopt this approach to ensure the reliability of their measurement results.

This explanation outlines the procedures for evaluating the uncertainty of each factor involved in $^{129}$I analysis, with the aim of enabling an understanding of various uncertainty assessment methods and evaluating uncertainty factors that should be considered at individual analytical institutions. Uncertainty factors are innumerable, including those with minor contributions, making it difficult to estimate uncertainty while considering all factors. Therefore, in practical operations, it is not always necessary to evaluate all factors; it is more practical to focus evaluations

on factors that make a significant contribution to the overall uncertainty. To assist in identifying factors that should be taken into account, we provide evaluation procedures and calculation examples for uncertainty in the actual analysis and measurement process.

## A.1 Basics of Uncertainty Assessment

In radionuclide analysis, the ultimate measurement quantity sought is the radioactivity concentration. However, no matter how accurately measurements are conducted or how thoroughly biases in all measured quantities are corrected, the measurement results are estimates and not the true values of the measured quantities. The measurement uncertainty is evaluated as a parameter expressing the reliability of these estimates. In the process from chemical analysis to radiation measurement, all input values used when calculating the radioactivity concentration are also estimates. We combine the uncertainties of all estimated values (input values) to calculate the measurement uncertainty of the target quantity, namely the radioactivity concentration.

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

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

$A$ : Radioactivity concentration

$f(x_1, x_2, x_3, \cdots, x_n)$: Function for deriving the radioactivity concentration

The combined standard uncertainty of the desired radioactivity concentration value is evaluated as the combined value of the uncertainties of all input values involved in deriving the radioactivity concentration. When each input value is completely independent (i.e., uncorrelated), their respective uncertainties are combined according to the following equation:

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

$u(A)$ : 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 value $x_i$ given by the differential coefficient $(\partial f/\partial x_i)$

In Equation (A.2), $c_i$ (sensitivity coefficient) represents how much the radioactivity concentration value $A$ changes in response to changes in each input value $x_1, x_2, x_3, \cdots, x_n$. For example, the change in the radioactivity concentration value $A$ caused by an infinitesimal change $\Delta x_i$ in the input value $x_i$ is given by $(\Delta A)_i = c_i \Delta x_i$. The change in the radioactivity concentration value $A$ reflecting the standard uncertainty of the input value $x_i$ is $|c_i| u(x_i)$.

Furthermore, when the number of variables $f$ is $m < n$

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

and the system is expressed solely by multiplication and division of $x_1$, $x_2$, $x_3$, ⋯, $x_n$, Equation (A.2) is equivalent to the following equation:

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

$\frac{u(A)}{A}$ : Relative combined standard uncertainty of the radioactivity concentration value $A$

$\frac{u(x_i)}{x_i}$ : Relative standard uncertainty of input value $x_i$

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 value. This explanation uses Equations (A.2) and (A.4) to evaluate the measurement uncertainty.

## A.2 Uncertainty Evaluation Procedure

The following text describes the procedure for evaluating uncertainty using the radiochemical analysis of soil, vegetable, polished rice, and seaweed samples as an example. If the net counting rate of $^{129}$I is measured using an LBC, the uncertainty in the radioactivity concentration can be determined as follows.

(1) The uncertainty factors are organized based on the calculation formula for the radioactivity concentration of $^{129}$I (hereinafter referred to as the “model equation”).

For instance, in the case of radiochemical analysis, the radioactivity concentration $A$ of $^{129}$I is determined using the following model equation:

$$A = \frac{r_n \times 100}{W_s \times Y \times \varepsilon} \quad \text{(A.5)}$$

$A$ : Radioactivity concentration of $^{129}$I in the sample (Bq/kg)

$W$s : Sample quantity (kg)

$Y$ : Recovery rate (%)

$\varepsilon$ : $^{129}$I counting efficiency (cps/Bq)

$r_n$ : $^{129}$I net counting rate (cps)

Various uncertainty factors can be considered for each item. An example of a budget sheet created to organize the uncertainty factors is shown in Table I.A.1. Notably, there may be factors not listed in Table I.A.1 that could also affect the measurement results.

(2) Evaluate the uncertainty for each factor

Uncertainty evaluation methods are classified into two types.

(i) Type A evaluation: It is a method for assessing uncertainty through the statistical analysis of a series of input values. For each factor, the standard deviation of the experiment is determined from repeated measurements and used as the standard uncertainty.

(ii) Type B evaluation: It is a method for assessing uncertainty through means other than statistical analysis of a series of input values. It involves evaluating each factor based on scientific judgment and using all available information regarding potential variations. The information available includes the following:

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

Not all sources of uncertainty contribute significantly to the uncertainty of the measurement result to be evaluated. Hence, evaluate the uncertainties of all factors individually, combine these uncertainties to determine their contribution to the overall uncertainty, and omit factors contributing minimally to the overall uncertainty in future measurements.

(3) Combine the uncertainties of individual factors to determine the uncertainty of the measurement result.

The relative combined standard uncertainty of the radioactivity concentration is determined as the square root of the sum of the squares of the relative standard uncertainties of each input value. The combined standard uncertainty of the radioactivity concentration is obtained by multiplying its relative combined standard uncertainty by the radioactivity concentration. The combined standard uncertainty represents the standard deviation associated with the measurement result. When it is necessary to analyze an interval expected to contain most values associated with the measurement, the expanded uncertainty is obtained by multiplying the combined standard uncertainty by the coverage factor $k$. The value of $k$ is determined based on the applied confidence level and the t-distribution[*150]. It is generally chosen to be between 2 and 3. In radioactivity concentration measurements, the distribution of measurement results can be considered normal, yielding $k = 2$ at a confidence level of approximately 95%. When reporting measurement results with uncertainty, clearly state whether the uncertainty is a combined standard uncertainty or an expanded uncertainty ($k = 2$–$3$).

[*150] For reference, see Appendix G of the following literature (Table G.2 is a t-distribution table):
今井秀孝 他: 測定における不確かさの表現のガイド [GUM]のハンドブック、日本規格協会出版
ISBN: 9784542307056 (2018)

Table I.A.1 shows an example of the calculation of the relative combined standard uncertainty. The overall relative combined standard uncertainty is 4.1% (with two significant figures). It consists of the uncertainty associated with the standard solution ($u_6$) and the uncertainty due to statistical counting.
One can see that the contribution of ($u_{10}$) is very large while that of the other items is small.

This indicates that under the same analysis and measurement conditions as in the calculation example, with the $^{129}$I radioactivity concentration remaining at or below the same level, it is practically acceptable to consider only the relative standard uncertainty ($u_6$) associated with the standard solution and the relative standard uncertainty ($u_{10}$) pertaining to the statistics of the count as 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 uncertainty of each factor. However, uncertainty factors whose contribution is one-tenth or less compared to the largest contributing uncertainty factor have a negligible effect on the final calculation result and can be practically disregarded. For example, when combining relative standard uncertainties of 4% and 0.4%, the result is $\sqrt{4^2 + 0.4^2}=\sqrt{16.16}=$ 4.02 %. Since the uncertainty is typically reported with 1–2 significant digits, this combination has little effect on the result.

In uncertainty assessment, it is crucial to reliably evaluate factors contributing significantly to uncertainty. Attempting to evaluate all uncertainty factors, including those with minor contributions, is impractical. In radiation measurements, the major sources of uncertainty include statistical uncertainty in counting and uncertainty in the assigned value of the standard radioactive source. In most cases, evaluating these factors is sufficient for practical purposes.

It should be noted that it is not necessary to evaluate all uncertainty factors listed in Table I.A.1 for every measurement. Items that fluctuate with each measurement, such as statistical uncertainty in counting, must be evaluated every time. However, other items need to be evaluated only at specific intervals, such as when equipment is updated, during maintenance inspections, or when changing reagent lots. In such a case, the relative combined standard uncertainty of measurement is obtained by combining the statistical uncertainty of the count (which varies from measurement to measurement) with other uncertainties (which do not vary from measurement to measurement).

Table I.A.1 Uncertainty budget sheet (example)

| Uncertainty factor※1 | Relative standard uncertainty | Calculated value※2 | Remarks |
|---|---|---|---|
| **A.3.1 Sample quantity ($Ws$)** | $\frac{u(Ws)}{Ws}$ | 0.011% | Relative standard uncertainty of (1) |
| (1) Weighing | $u_1$ | 0.011% | |
| **A.3.2 Recovery rate ($Y$)** | $\frac{u(Y)}{Y}$ | 0.52% | Combine the relative standard uncertainties of (2)–(4) with the relative standard uncertainty of (6). |
| (2) Quantity of $^{127}$I added as a carrier | $u_2$ | 0.18% | Combined standard uncertainty of $u_2$–$u_4$ ＝0.036 mg Relative combined standard uncertainty of (2)–(4) ＝0.18% |
| (3) Measurement of $^{127}$I in samples | $u_3$ | 1.4% | |
| (4) Weight of palladium iodide | $u_4$ | 0.49% | |
| (6) Amount of $^{127}$I determined by recovery rate measurement | $u_5$ | 0.49% | |
| A.3.3 Counting efficiency ($\varepsilon$) for $^{129}$I | $\frac{u(\varepsilon)}{\varepsilon}$ | 3.1% | Combined relative standard uncertainty for (1)–(4). |
| (1) Standard solution | $u_6$ | 3.0% | |
| (2) Aliquoting of the standard solution | $u_7$ | 0.074% | |
| (3) Measurement of samples for generating efficiency curves | $u_8$ | 0.47% | |
| (4) Recovery rate of samples determined for generating efficiency curves | $u_9$ | 0.38% | |
| **A.3.4 $^{129}$I net counting rate ($r_n$)** | $\frac{u(r_n)}{r_n}$ | 2.6% | Combine the relative standard uncertainties of (1) and (2). |
| (1) Count statistics | $u_{10}$ | 2.6% | Evaluate for each measurement |
| (2) Variation in the measurement system | $u_{11}$ | 0.35% | |
| **Relative combined standard uncertainty※3** | $\frac{u(A)}{A}$ | 4.1% | Evaluate for each measurement |

※1 The numbers preceding each uncertainty factor correspond to the sections referenced in Section A.3.

※2 For convenience, intermediate values are rounded off. However, actual calculations are performed without rounding off.

※3 The number of significant digits for the relative combined standard uncertainty should not exceed two.

[Method for Identifying Factors to Be Considered in Analysis]

- In this explanation, factors with small contributions are intentionally included to aid in mastering evaluation methods for various factors. However, when actually performing uncertainty evaluation, it is advisable to prioritize the evaluation of the uncertainty associated with the standard solution and the uncertainty arising from statistical counting as the major relative standard uncertainties within the overall system ("A.3.3 (1) and A.3.4 (1)").
- To reliably evaluate factors contributing significantly to uncertainty, it is advisable to refer to the uncertainty values for each factor in this table, assess any additional factors likely to introduce substantial uncertainty, combine them with the uncertainty from statistical counting, and then determine whether these uncertainty factors should be considered.
- Regarding factors other than statistical uncertainty in counting, evaluation can be performed at times such as equipment updates, maintenance inspections, or reagent lot changes.

## A.3 Example of Uncertainty Calculation

In the example in Section A.2, the calculation methods for each factor shown in Table I.A.1 are provided only for reference.

During the calculation of the uncertainty for each factor, numerical values are not rounded off. Rounding is performed only once at the final step when determining the relative combined standard uncertainty[*151].

The radioactivity concentration value $A$ of $^{129}$I is calculated using the following model equation derived from Equation (A.5):

$$A = \frac{r_n \times 100}{W_s \times Y \times \varepsilon}$$

$A$ : Radioactivity concentration of $^{129}$I in the sample (Bq/kg)

$W_s$ : Sample quantity (kg)

$Y$ : Recovery rate (%)

$\varepsilon$ : $^{129}$I counting efficiency (cps/Bq)

$rn$ : $^{129}$I Net counting rate (cps)

The relative combined standard uncertainty of the radioactivity concentration value $A$ for $^{129}$I

[*151] For convenience, intermediate values are shown as rounded-off values (although the actual calculations are performed without rounding).

is determined by combining the relative standard uncertainties of all parameters in the model equation (sample quantity $Ws$, recovery rate $Y$, $^{129}$I counting efficiency $\varepsilon$, and net counting rate $rn$ for $^{129}$I).

Here, we define the combined standard uncertainty of $A$ as $u(A)$ and the relative combined standard uncertainty as $\frac{u(A)}{A}$. Further, we establish other parameters similarly.

Applying the relative standard uncertainties $(\frac{u(x_i)}{x_i})$ of the input quantities $x_1$, $x_2$, $x_3$, ⋯, $x_n$ in Equation (A.4) to each parameter in the model equation yields the following expression:

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

To determine $\frac{u(A)}{A}$, the relative standard uncertainties of the sample quantity $W$, recovery rate $Y$, counting efficiency $\varepsilon$ of $^{129}$I, and net counting rate $r_n$ of $^{129}$I are evaluated as described in A.3.1–A.3.4. These relative standard uncertainties are then combined as described in A.3.5 using Equation (A.6).

### A.3.1 Uncertainty of the Sample Quantity $W_s$ $(\frac{u(W_s)}{W_s})$

For soil, vegetable, polished rice, or seaweed samples, the uncertainty factor for the sample quantity $W_s$ is considered to be the uncertainty of weighing. Here, the relative standard uncertainty of weighing is defined as $u_1$.

(1) Uncertainty of weighing ($u_1$)

Determination of the uncertainty of weighing is dependent on whether the calibration certificate of the electronic balance used specifies its uncertainty.

Furthermore, the heterogeneous distribution of radionuclides within the sample affects the measured values; however, it is difficult to estimate their uncertainty. Therefore, although it is not necessary to evaluate the homogeneity of the sample, the sample must be thoroughly mixed and brought to a uniform state before weighing.

a) When uncertainty is indicated on the calibration certificate

Use the uncertainty stated on the calibration certificate for the electronic balance. When the stated uncertainty is not a relative value, the relative standard uncertainty of weighing ($u_1$) is determined using the following equation:

$$u_1 = \frac{u(W)}{W} \times 100\ (\%) \quad \text{(A.7)}$$

$u(W)$ : Uncertainty of weight (g)

$W$ : Weight (g)

b) When the calibration certificate does not specify uncertainty information

If the uncertainty information is not stated, the relative standard uncertainty of weighing ($u_1$) is obtained by combining the relative standard uncertainty pertaining to the rounding of the weight ($u_{1.1}$) and the relative standard uncertainty pertaining to the repeatability of weighing ($u_{1.2}$). The uncertainty obtained by combining these factors pertains only to the weighing process. The measurement uncertainty during calibration is negligible and need not be considered. However, if there are other significant sources of uncertainty, they should be considered.

1) Uncertainty due to the rounding of weights ($u_{1.1}$)

If the readability (minimum scale interval) of an electronic balance is denoted as $l$, then at the zero point and the weight, the readout follows a rectangular distribution with upper and lower limits of $\pm l/2$. Combining these two distributions yields a triangular distribution with upper and lower bounds of $\pm l$; therefore, $u1.1$ can be

$$u_{1.1} = \frac{l}{\sqrt{6} \times W} \times 100\ (\%) \tag{A.8}$$

$l$ : Readability (g)

$W$ : Weight (g)

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

Using weights with masses approximately equal to that of the sample, perform 10 repeated measurements, calculate the mean and standard deviation, and determine the relative standard uncertainty. When the mean of $n$ measurements is used as the sample quantity, $u_1.2$ is calculated using the following equation:

$$u_{1.2} = \frac{W_{\mathrm{STD}}}{\bar{W}} \times \frac{1}{\sqrt{n}} \times 100\ (\%) \tag{A.9}$$

$\bar{W}$ : Mean of repeated measurements (g)

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

$n$ : Number of repetitions

3) Combination of uncertainties ($u_1$)

Combine $u_{1.1}$ and $u_{1.2}$ to obtain $u_1$:

$$u_1 = \sqrt{(u_{1.1})^2 + (u_{1.2})^2} \tag{A.10}$$

Calculation Example: (When uncertainty is not stated on the calibration certificate)

When using an electronic balance with a readability of 0.01 g and weight of 100.10 g, determine $u_{1.1}$ using Equation (A.8) as follows:

$$u_{1.1} = \frac{l}{\sqrt{6} \times \bar{W}} \times 100 = \frac{0.01}{\sqrt{6} \times 100.10} \times 100 = 0.0041\ \%$$

When the mean of repeated measurements is 100.23 g, standard deviation is 0.01 g, and number of measurements per sample is 1, $u_{1.2}$ is determined using Equation (A.9) as

follows:

$$u_{1.2} = \frac{W_{STD}}{\bar{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.01}{100.23} \times \frac{1}{\sqrt{1}} \times 100 = 0.010\,\%$$

Then, obtain $u_1$ using Equation (A.10) as follows:

$$u_1 = \frac{u(\bar{W})}{\bar{W}} = \sqrt{(u_{1.1})^2 + (u_{1.2})^2} = \sqrt{0.0041^2 + 0.010^2} = 0.011\,\%$$

### A.3.2 Uncertainty of the Recovery Rate $\left(\frac{u(Y)}{Y}\right)$

The recovery rate $Y$ of $^{127}$I in $^{129}$I measurements is calculated using the following equation:

$$Y = \frac{W_2}{W_1 + C_I \times W_s} \times 100\ (\%) \qquad \text{(A.11)}$$

$W_1$ : Amount of $^{127}$I added as a carrier (mg)

$C_I$ : $^{127}$I concentration in the sample (mg/g)

$W_s$ : Sample quantity (g)

$W_2$ : Amount of $^{127}$I determined by recovery rate measurement (mg)

Here, the relative standard uncertainties of $W_1$, $C_I$, $W$s, and $W_2$ are defined as follows:

$\frac{u(W_1)}{W_1}(=u_2)$ : Relative standard uncertainty of $W_1$

$\frac{u(C_I)}{C_I}(=u_3)$ : Relative standard uncertainty of $C_I$

$\frac{u(W_s)}{W_s}(=u_4)$ : Relative standard uncertainty of $W$s

$\frac{u(W_2)}{W_2}(=u_5)$ : Relative standard uncertainty of $W_2$

Let $W_1 + C_I \times W$s = Z. Then, Equation (A.11) can be expressed as follows:

$$Y = \frac{W_2}{W_1 + C_I \times W_s} = \frac{W_2}{Z}$$

Therefore, $\frac{u(Y)}{Y}$ is obtained by composing $\frac{u(Z)}{Z}$ and $\frac{u(W_2)}{W_2}$ (=$u_5$) using the following equation:

$$\frac{u(Y)}{Y} = \sqrt{\left(\frac{u(Z)}{Z}\right)^2 + \left(\frac{u(W_2)}{W_2}\right)^2} \qquad \text{(A.12)}$$

Here, after obtaining $\frac{u(Z)}{Z}$ in (1)–(5), we determine $u(W_2)$ (=$u$) in (6). Then, we obtain $u(Y)$ by combining $\frac{u(Z)}{Z}$ and $\frac{u(W_2)}{W_2}$.

(1) Uncertainty of $Z$ $\frac{u(Z)}{Z}$

$Z$ (= $W_1 + C_I \times W$s) consists of a product term ($C_I \times W$s) and a sum term ($W_1 + C_I \times W$s). The combined standard uncertainty of the product part is calculated, in accordance with Equation (A.4), as the square root of the sum of the squares of the relative standard uncertainties of $C_I$ and $W$s. Further, the combined standard uncertainty of the sum part is calculated, in accordance with

Equation (A.2), as the square root of the sum of the squares of the standard uncertainties of $W_1$ and $C_I \times W_s$.

First, the composite standard uncertainty of the product term ($C_I \times W_s$) is determined as follows:

$$(C_I \pm u(C_I)) \times (W_s \pm u(W_s))$$

$$= (C_I \times W_s) \pm (C_I \times W_s) \times \sqrt{\left(\frac{u(C_I)}{C_I}\right)^2 + \left(\frac{u(W_s)}{W_s}\right)^2}$$

$$= (C_I \times W_s) \pm \left(\sqrt{\left({C_I}^2 \times {W_s}^2 \times \left(\frac{u(C_I)}{C_I}\right)^2\right) + \left({C_I}^2 \times {W_s}^2 \times \left(\frac{u(W_s)}{W_s}\right)^2\right)}\right)$$

$$= (C_I \times W_s) \pm \left(\sqrt{{W_s}^2 \times (u(C_I))^2 + {C_I}^2 \times (u(W_s))^2}\right)$$

Next, combine the combined standard uncertainty of $W_1$ with the combined standard uncertainty of $C_I \times W_s$:

$$(W_1 \pm (u(W_1)) + \left((C_I \times W_s) \pm \left(\sqrt{{W_s}^2 \times (u(C_I))^2 + {C_I}^2 \times (u(W_s))^2}\right)\right)$$

$$= \left(W_1 + (C_I \times W_s)\right) \pm \left(\sqrt{(u(W_1))^2 + \left(\sqrt{{W_s}^2 \times (u(C_I))^2 + {C_I}^2 \times (u(W_s))^2}\right)^2}\right)$$

$$= \left(W_1 + (C_I \times W_s)\right) \pm \sqrt{(u(W_1))^2 + {W_s}^2 \times (u(C_I))^2 + {C_I}^2 \times (u(W_s))^2}$$

Then, $u(Z)$ is obtained using the following equation:

$$u(Z) = \sqrt{(u(W_1))^2 + {W_s}^2 \times (u(C_I))^2 + {C_I}^2 \times (u(W_s))^2} \quad \text{(A.13)}$$

Next, calculate $Z$ and divide $u(Z)$ by $Z$ to obtain $\frac{u(Z)}{Z}$.

The uncertainty associated with an analysis conducted under the following conditions is described as a calculation example.

$W_1$ = 20.00 mg

$C$I = 0.65 mg/g

$W$s = 0.50 g

$W_2$ = 19.80 mg

$Z$ is calculated using the above values as follows:

$$Z = W_1 + C_I \times W_s = 20.00 \text{ mg} + 0.65 \text{ mg/g} \times 0.50 \text{ g} = 20.3 \text{ mg}$$

(2) Uncertainty in the amount of $^{127}$I added as a carrier ($u_2$)

The carrier solution is prepared by dissolving sodium iodide in pure water and then adjusting

the volume to a fixed level. Therefore, $u_2$ is determined by combining the relative standard uncertainties pertaining to the weight of sodium iodide ($u_{2.1}$), purity of sodium iodide ($u_{2.2}$), dilution of the carrier solution ($u_{2.3}$), and addition of the carrier solution ($u_{2.4}$).

1) Uncertainty due to the weighing of sodium iodide ($u_{2.1}$)

Perform the same calculation as in "A.3.1 Uncertainty of the Sample Quantity."

2) Uncertainty due to the purity of sodium iodide ($u_{2.2}$)

The purity of sodium iodide, when considered to have a concentration range centered on the purity $R$% indicated on the reagent bottle, can be expressed as follows. Here, the maximum purity value is assumed to be 1 (100%), and the range from the minimum to the central purity value is taken to be equal to the range from the maximum to the central purity value.

Maximum value : 1

Median value : $R$

Minimum value : $R-(1-R)=2R-1$

Purity tolerance : $\frac{1-(2R-1)}{2}$

Assuming a rectangular distribution within the above concentration range, $u_{2.2}$ can be calculated using the following equation:

$$u_{2.2}=\frac{1-(2R-1)}{2\sqrt{3}\times R}\times 100\ (\%) \qquad \text{(A.14)}$$

3) Uncertainty in the dilution of the carrier solution ($u_{2.3}$)

A volumetric flask is used to dilute the carrier solution. Therefore, $u_{2.3}$ is determined by combining the relative standard uncertainties pertaining to the volumetric flask capacity ($u_{2.3.1}$) and repeatability ($u_{2.3.2}$).

3-1) Uncertainty pertaining to the capacity of the volumetric flask ($u_{2.3.1}$)

Since the tolerance range of the volumetric flask capacity follows a rectangular distribution, $u_{2.3.1}$ is calculated using the following equation:

$$u_{2.3.1}=\frac{V_i}{\sqrt{3}\times V}\times 100\ (\%) \qquad \text{(A.15)}$$

$V$ : Capacity of the volumetric flask (mL)

$Vi$ : Tolerance for the volumetric flask capacity (mL)

3-2) Uncertainty due to the repeatability of the volumetric flask ($u_{2.3.2}$)

Using an electronic balance, measure the mass of pure water filled to the calibration mark in a volumetric flask in ten repeated trials and then calculate the mean and standard deviation. When adopting the mean from n measurements, $u_{2.3.2}$ is calculated using the following equation:

$$u_{2.3.2} = \frac{W_{\mathrm{STD}}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100\ (\%) \quad \text{(A.16)}$$

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

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

$n$ : Number of repetitions

3-3) Combination of uncertainties ($u_{2.3}$)

Combine $u_{2.3.1}$ and $u_{2.3.2}$ to obtain $u_{2.3}$.

$$u_{2.3} = \sqrt{(u_{2.3.1})^2 + (u_{2.3.2})^2} \quad \text{(A.17)}$$

4) Uncertainty in the addition of the carrier solution ($u_{2.4}$)

When adding the carrier solution, it is necessary to consider the uncertainty due to the calibration of the micropipette used ($u_{2.4.1}$) and the uncertainty due to the repeatability of the same pipette ($u_{2.4.2}$)[*152,*153,*154]. In addition, the tolerance of the volumetric instrument, etc. can be accounted for[*155].

4-1) Uncertainty due to the calibration of the micropipette ($u_{2.4.1}$)

The method for obtaining $u_{2.4.1}$ is dependent on whether a calibration certificate for the micropipette used is available.

a) Calibration certificate is available

Using the calibration value stated on the calibration certificate of the micropipette being used and the expanded uncertainty at the time of calibration, $u_{2.4.1}$ is determined using the following equation:

$$u_{2.4.1} = \frac{U_{pipette}/_{k}}{V_{pipette}} \times 100\ (\%) \quad \text{(A.18)}$$

$V_{pipette}$ : Calibration value of the micropipette (mL)

$k$ : Coverage factor

$U_{pipette}$ : Expanded uncertainty during micropipette calibration (mL)

b) Calibration certificate is not available

Calculate $u_{2.4.1}$ using the micropipette's tolerance by assuming a rectangular distribution and using the following equation:

$$u_{2.4.1} = \frac{V_{i\ pipette}}{\sqrt{3} \times V_{pipette}} \times 100\ (\%) \quad \text{(A.19)}$$

*152 K. Shirono et al.: Evaluation of "method uncertainty" in the calibration of piston pipettes (micropipettes) using the gravimetric method in accordance with the procedure of ISO 8655, Accreditation and Quality Assurance, 19, 377-389 (2014)

*153 K. Shirono et al.: Evaluation of reproducibility uncertainty in micropipette calibrations for non-nominal volumes through an interlaboratory study, Accreditation and Quality Assurance, 26, 27-39 (2021)

*154 城野克広、マイクロピペットによる体積測定の精確さの管理、計測標準と計量管理, 73(1), pp. 2-9 (2023)

*155 JIS K 0970: ピストン式ピペット(2013)

$V_{pipette}$ : Micropipette volume (mL)

$Vi_{\ pipette}$ : Micropipette capacity tolerance (mL)

4-2) Uncertainty due to micropipette repeatability ($u_{2.4.2}$)

Using a micropipette, aliquot pure water with an amount equal to that of the carrier solution.

Then, measure its mass 10 times using an electronic balance. Next, calculate the mean and standard deviation. When the mean of $n$ measurements is used as the sample quantity, $u_{2.4.2}$ is calculated using the following equation:

$$u_{2.4.2} = \frac{W_{\mathrm{STD}}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100\ (\%) \qquad \text{(A.20)}$$

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

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

$n$ : Number of repetitions

4-3) Combination of uncertainties ($u_{2.4}$)

Combine $u_{2.4.1}$ to $u_{2.4.2}$ to obtain $u_{2.4}$:

$$u_{2.4} = \sqrt{(u_{2.4.1})^2 + (u_{2.4.2})^2} \qquad \text{(A.21)}$$

5) Combination of uncertainties ($u_2$)

Combine $u_{2.1}$ to $u_{2.4}$ to obtain $u_2$:

$$u_2 = \sqrt{(u_{2.1})^2 + (u_{2.2})^2 + (u_{2.3})^2 + (u_{2.4})^2} \qquad \text{(A.22)}$$

[Calculation Example]

During the preparation of the iodine carrier solution, determine $u_{2.1.1}$ from Equation (A.8) as follows when the weighed amount of sodium iodide is 1.0005 g on an electronic balance with a readability of 0.0001 g:

$$u_{2.1.1} = \frac{l}{\sqrt{6} \times W} \times 100 = \frac{0.0001}{\sqrt{6} \times 1.0005} \times 100 = 0.0041\ \%$$

Next, when the mean of repeated measurements is 10.0110 g, standard deviation is 0.0012 g, and number of measurements per sample is 1, obtain $u_{2.1.2}$ from Equation (A.9) as follows:

$$u_{2.1.2} = \frac{W_{\mathrm{STD}}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.0012}{10.0110} \times \frac{1}{\sqrt{1}} \times 100 = 0.012\ \%$$

Combine $u_{2.1.1}$ and $u_{2.1.2}$ and obtain $u_{2.1}$ from Equation (A.10) as follows:

$$u_{2.1} = \sqrt{(u_{2.1.1})^2 + (u_{2.1.2})^2} = \sqrt{0.0041^2 + 0.012^2} = 0.013\ \%$$

When the purity of sodium iodide is 99.95%, calculate $u_{2.2}$ from Equation (A.14) as follows:

$$u_{2.2} = \frac{1 - (2R - 1)}{2\sqrt{3} \times R} \times 100 = \frac{1 - (2 \times 0.9995 - 1)}{2\sqrt{3} \times 0.9995} \times 100 = 0.029\ \%$$

Then, when preparing the carrier solution in a 500 mL volumetric flask with a tolerance of 0.25 mL, obtain $u_{2.3.1}$ using Equation (A.15) as follows:

$$u_{2.3.1} = \frac{V_i}{\sqrt{3} \times V} \times 100 = \frac{0.25}{\sqrt{3} \times 500} \times 100 = 0.029\,\%$$

When the mean of repeated measurements of the volumetric flask is 500.08 g, standard deviation is 0.18 g, and number of sample measurements is 1, calculate $u_{2.3.2}$ from Equation (A.16) as follows:

$$u_{2.3.2} = \frac{W_{STD}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.18}{500.08} \times \frac{1}{\sqrt{1}} \times 100 = 0.036\,\%$$

Combine $u_{2.3.1}$ and $u_{2.3.2}$ to obtain $u_{2.3}$ from Equation (A.17) as follows:

$$u_{2.3} = \sqrt{(u_{2.3.1})^2 + (u_{2.3.2})^2} = \sqrt{0.029^2 + 0.036^2} = 0.046\,\%$$

When the calibration value stated on the calibration certificate for the micropipette used to add the carrier solution is 1000.0 $\mu$L, expanded uncertainty at calibration is 0.8 $\mu$L, and coverage factor is 2, determine $u_{2.4.1}$ using Equation (A.18) as follows:

$$u_{2.4.1} = \frac{U_{pipette}/_k}{V_{pipette}} \times 100 = \frac{0.8/2}{1000.0} \times 100 = 0.040\,\%$$

When the mean of repeated measurements is 0.9974 g, standard deviation is 0.0017 g, and the number of measurements per sample is 1, obtain $u_{2.4.2}$ from Equation (A.20) as follows:

$$u_{2.4.2} = \frac{W_{STD}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.0017}{0.9974} \times \frac{1}{\sqrt{1}} \times 100 = 0.17\,\%$$

Then, obtain the uncertainty of the carrier solution addition ($u_{2.4}$) from Equation (A.21) as follows:

$$u_{2.4} = \sqrt{(u_{2.4.1})^2 + (u_{2.4.2})^2} = \sqrt{0.040^2 + 0.17^2} = 0.17\,\%$$

Finally, obtain $u_2$ from Equation (A.22) as follows:

$$u_2 = \sqrt{(u_{2.1})^2 + (u_{2.2})^2 + (u_{2.3})^2 + (u_{2.4})^2}$$
$$= \sqrt{0.013^2 + 0.029^2 + 0.046^2 + 0.17^2} = 0.18\,\%$$

(3) Uncertainty in the measurement of $^{127}$I in the sample ($u_3$)

The following describes how to determine the uncertainty when measuring the concentration of $^{127}$I ($CI$) in a sample using an ion meter or via ICP–MS. $u_3$ is obtained by combining the uncertainty pertaining to the weighing of the measurement sample ($u_{3.1}$), uncertainty pertaining to the dilution of the $^{127}$I measurement sample ($u_{3.2}$), uncertainty of the calibration curve ($u_{3.3}$), and relative standard uncertainty of the calibration solution ($u_{3.4}$).

1) Uncertainty pertaining to the weighing the measurement sample ($u_{3.1}$)

The uncertainty pertaining to sample weighing is determined in the same manner as described in "A.3.1 Uncertainty of the Sample Quantity." If the calibration certificate does not specify uncertainty, $u_{3.1}$ is determined by combining the relative standard uncertainties pertaining to the rounding of the weight ($u_{3.1.1}$) and the repeatability of weighing ($u_{3.1.2}$).

[Calculation Example]

When using an electronic balance with a readability of 0.01 mg and the weighed amount is 1000.34 mg, obtain $u_{3.1.1}$ from Equation (A.8) as follows

$$u_{3.1.1} = \frac{l}{\sqrt{6} \times W} \times 100 = \frac{0.01}{\sqrt{6} \times 1000.34} \times 100 = 0.00041\ \%$$

When the mean of repeated measurements performed using an electronic balance is 1000.66 mg, standard deviation is 0.09 mg, and number of sample measurements is 1, obtain $u_{3.1.2}$ from Equation (A.9) as follows:

$$u_{3.1.2} = \frac{W_{STD}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.09}{1000.66} \times 100 \times \frac{1}{\sqrt{1}} = 0.0090\ \%$$

Then, combine $u_{3.1.1}$ and $u_{3.1.2}$ to obtain $u_{3.1}$:

$$u_{3.1} = \sqrt{(u_{3.1.1})^2 + (u_{3.1.2})^2} = \sqrt{0.00041^2 + 0.0090^2} = 0.0090\ \%$$

2) Uncertainty pertaining to the dilution of the $^{127}$I measurement sample ($u_{3.2}$)

A volumetric flask and micropipette are used to dilute the $^{127}$I measurement sample solution. Therefore, $u_{3.2}$ is determined by combining the relative standard uncertainties pertaining to the volumetric flask capacity ($u_{3.2.1}$) and the micropipette volume ($u_{3.2.2}$), similar to previously mentioned $u_{2.3}$ and $u_{2.4}$.

2-1) Uncertainty of the volumetric flask capacity ($u_{3.2.1}$)

$u_{3.2.1}$ is obtained by combining the relative standard uncertainties pertaining to the volumetric flask capacity ($u_{3.2.1.1}$) and the repeatability of the volumetric flask ($u_{3.2.1.2}$), similar to $u_{2.3}$.

2-2) Uncertainty of the micropipette ($u_{3.2.2}$)

$u_{3.2.2}$ is obtained by combining the relative standard uncertainties pertaining to pipette calibration ($u_{3.2.2.1}$) and repeatability ($u_{3.2.2.2}$), similar to $u_{2.4}$.

2-3) Combination of uncertainties ($u_{3.2}$)

Combine $u_{3.2.1}$ and $u_{3.2.2}$ to obtain $u_{3.2}$:

$$u_{3.2} = \sqrt{(u_{3.2.1})^2 + (u_{3.2.2})^2} \quad \text{(A.23)}$$

[Calculation Example]

When preparing the carrier solution in a 100 mL volumetric flask with a tolerance of 0.05 mL, obtain $u_{3.2.1.1}$ from Equation (A.15) as follows:

$$u_{3.2.1.1} = \frac{V_i}{\sqrt{3} \times V} \times 100 = \frac{0.05}{\sqrt{3} \times 100} \times 100 = 0.029\ \%$$

When the mean of repeated measurements is 100.03 g, standard deviation is 0.04 g, the number of measurements per sample is 1, obtain $u_{3.2.1.2}$ from Equation (A.16) as follows:

$$u_{3.2.1.2} = \frac{W_{STD}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.04}{100.03} \times \frac{1}{\sqrt{1}} \times 100 = 0.040\ \%$$

Then, obtain $u_{3.2.1}$ from Equation (A.17) as follows:

$$u_{3.2.1} = \sqrt{(u_{3.2.1.1})^2 + (u_{3.2.1.2})^2} = \sqrt{0.029^2 + 0.040^2} = 0.049\ \%$$

When the calibration value stated on the calibration certificate for the micropipette used to add the carrier solution is 1000.0 $\mu$L, expanded uncertainty during calibration is 0.8 $\mu$L, and coverage factor is 2, determine $u_{3.2.2.1}$ using Equation (A.18) as follows:

$$u_{3.2.2.1} = \frac{U_{pipette}/_{k}}{V_{pipette}} \times 100 = \frac{0.8/2}{1000.0} \times 100 = 0.040\,\%$$

When the mean of repeated measurements using the micropipette is 0.9974 g, standard deviation is 0.0017 g, and number of sample measurements is 1, obtain $u_{3.2.2.2}$ from Equation (A.20) as follows:

$$u_{3.2.2.2} = \frac{W_{\mathrm{STD}}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.0017}{0.9974} \times \frac{1}{\sqrt{1}} \times 100 = 0.17\,\%$$

Then, obtain the uncertainty pertaining to carrier solution addition ($u_{3.2.2}$) from Equation (A.21) as follows:

$$u_{3.2.2} = \sqrt{(u_{3.2.2.1})^2 + (u_{3.2.2.2})^2} = \sqrt{0.040^2 + 0.17^2} = 0.17\,\%$$

Finally, obtain $u_{3.2}$ from Equation (A.23) as follows:

$$u_{3.2} = \sqrt{(u_{3.2.1})^2 + (u_{3.2.2})^2} = \sqrt{0.049^2 + 0.17^2} = 0.18\,\%$$

3) Uncertainty of the calibration curve ($u_{3.3}$)

When a calibration curve is generated using the least squares method from the results of measuring $n$ standard solutions of different concentrations and a linear equation of the form $y = ax + b$ is obtained, the uncertainty is determined as follows. Strictly speaking, evaluation should be performed for each measurement. However, the impact of differences in uncertainty between individual calibration curves on the final uncertainty is negligible. Therefore, unless there are changes in instrument calibration or conditions, it is not always necessary to evaluate uncertainty for each measurement.

The standard uncertainty of the calibration curve $u(C_{\mathrm{f}})$ is calculated as the difference between the actual measured intensity $y_{\mathrm{i}}$ of the standard solution and the estimated intensity $y_{\mathrm{est}}$ obtained by substituting concentration $x$ into the equation $y = ax + b$, followed by dividing the largest value among these differences by the slope $a$[*156].

$$u(C_{\mathrm{f}}) = \frac{|\mathrm{MAX}(y_{\mathrm{i}} - y_{\mathrm{est}})|}{a} \tag{A.24}$$

$y_{\mathrm{i}}$ : Actual intensity obtained by measuring the standard solution

$y_{\mathrm{est}}$ : Estimated intensity $y$ obtained by substituting concentration $x$ into $y = ax + b$.

Thus, $u_{3.3}$ is obtained using the following equation:

$$u_{3.3} = \frac{u(C_{\mathrm{f}})}{C_{\mathrm{f}}} \times 100\ (\%) \tag{A.25}$$

[*156] This evaluation method is simple but overestimates uncertainty. For more appropriate uncertainty evaluation, refer to the following material, which describes other methods. Accreditation Center, National Institute of Technology and Evaluation: Evaluation of Measurement Uncertainty in JCSS Calibration - Estimation of Uncertainty Using the Interpolation Correction Method, JCG200S21-02 (2022).

$Cf$ : Concentration of the measurement sample

[Calculation Example]

Assume that measurements are performed using six standard solutions with concentrations ranging from 0 µg/L to 10.0 µg/L (Table I.A.2) and the linear equation obtained is y = 0.01465x + 0.00139.

Table I.A.2 Calibration measurement results

| | Standard 1 | Standard 2 | Standard 3 | Standard 4 | Standard 5 | Standard 6 |
|---|---|---|---|---|---|---|
| $x$: Concentration | 0 | 0.1 | 0.5 | 1 | 5 | 10 |
| $y_i$: Intensity※ | 0.00124 | 0.00308 | 0.00955 | 0.01566 | 0.07352 | 0.14839 |
| $y_{est}$ | 0.00138 | 0.00285 | 0.00871 | 0.01603 | 0.07462 | 0.14785 |
| $y_i - y_{est}$ | -0.00015 | 0.00023 | 0.00085 | -0.00037 | -0.00110 | 0.00054 |

※Values corrected using an internal standard

From Equation (A.24), obtain $u(C_f)$. For determining $y_i - y_{est}$, use the value of standard 5, for which the difference between the calibration curve and the measured point is the greatest.

$$u(C_f) = \frac{|\mathrm{MAX}(y_i - y_{est})|}{a} = \frac{|-0.00110|}{0.01465} = 0.07509$$

Then, for a measured sample concentration of 6 µg/L, obtain $u_{3.3}$ from Equation (A.25) as follows:

$$u_{3.3} = \frac{u(C_f)}{C_f} \times 100 = \frac{0.07509}{6} \times 100 = 1.3\ \%$$

4) Uncertainty of the calibration solution ($u_{3.4}$)

The calibration solution is prepared by diluting the undiluted calibration solution stock (either a commercially available standard solution or a solution prepared by dissolving sodium iodide). Therefore, $u_{3.4}$ is determined by combining the relative standard uncertainties pertaining to the undiluted calibration solution ($u_{3.4.1}$) and the dilution of the calibration solution ($u_{3.4.2}$).

4-1) Uncertainty of the Calibration Solution Stock ($u_{3.4.1}$)

a) When diluting commercially available standard solutions

Use the expanded uncertainty stated in the standard solution's certificate of analysis. Let the expanded uncertainty of the standard solution be $U\%$ and the coverage factor be $k$. Then, $u_{3.4.1}$ is determined using the following equation:

$$u_{3.4.1} = \frac{U}{k}(\%) \qquad \text{(A.26)}$$

b) When preparing the standard solution using sodium iodide

Since the standard solution is prepared by dissolving sodium iodide in pure water, the uncertainty in the weighing of sodium iodide ($u_{3.4.1.a}$), relative standard uncertainty of sodium iodide purity ($u_{3.4.1.b}$), and relative standard uncertainty of the volumetric flask ($u_{3.4.1.c}$) are combined to determine $u_{3.4.1.}$

[Calculation Example]

When preparing calibration solutions, determine the uncertainty due to rounding the weighed amount of sodium iodide ($u_{3.4.1.a1}$), e.g., 1.0002 g as per an electronic balance with a readability of 0.0001 g, using Equation (A.8) as follows:

$$u_{3.4.1.a1} = \frac{l}{\sqrt{6} \times W} \times 100 = \frac{0.0001}{\sqrt{6} \times 1.0002} \times 100 = 0.0041\,\%$$

When the mean of repeated measurements is 1.0003 g, standard deviation is 0.0002 g, and number of measurements per sample is 1, the uncertainty due to the repeatability of weighing ($u_{3.4.1.a2}$) is determined using Equation (A.9) as follows:

$$u_{3.4.1.a2} = \frac{W_{STD}}{W} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.0002}{1.0003} \times \frac{1}{\sqrt{1}} \times 100 = 0.020\,\%$$

The uncertainty due to the weighing of sodium iodide ($u_{3.4.1.a}$) is obtained from Equation (A.10) as follows:

$$u_{3.4.1.a} = \sqrt{0.0041^2 + 0.020^2} = 0.020\,\%$$

Then, obtain the uncertainty pertaining to the purity of sodium iodide ($u_{3.4.1.b}$), e.g., when the purity is 99.995%, from Equation (A.14) as follows:

$$u_{3.4.1.b} = \frac{1 - (2R - 1)}{2\sqrt{3} \times R} \times 100 = \frac{1 - (2 \times 0.99995 - 1)}{2\sqrt{3} \times 0.99995} \times 100 = 0.0029\,\%$$

When using a 100 mL volumetric flask with a tolerance of 0.1 mL to prepare the undiluted calibration solution, determine the uncertainty of the volumetric flask capacity ($u_{3.4.1.c1}$) using Equation (A.15) as follows:

$$u_{3.4.1.c1} = \frac{V_i}{\sqrt{3} \times V} \times 100 = \frac{0.1}{\sqrt{3} \times 100} \times 100 = 0.058\,\%$$

When the mean of repeated measurements is 100.05 g, standard deviation is 0.03 g, and number of measurements per sample is 1, the uncertainty due to the repeatability of the volumetric flask ($u_{3.4.1.c2}$) is determined using Equation (A.16) as follows:

$$u_{3.4.1.c2} = \frac{W_{STD}}{W} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.03}{100.05} \times \frac{1}{\sqrt{1}} \times 100 = 0.030\,\%$$

Then, $u_{3.4.1.c}$ is determined from Equation (A.17) as follows:

$$u_{3.4.1.c} = \sqrt{0.058^2 + 0.030^2} = 0.065\,\%$$

Combine $u_{3.4.1.a}$–$u_{3.4.1.c}$ and determine the uncertainty of the undiluted calibration solution ($u_{3.4.1}$):

$$u_{3.4.1} = \sqrt{(u_{3.4.1.a})^2 + (u_{3.4.1.b})^2 + (u_{3.4.1.c})^2}$$
$$= \sqrt{0.020^2 + 0.0029^2 + 0.065^2} = 0.068\,\%$$

4-2) Uncertainty pertaining to the dilution of the calibration solution ($u_{3.4.2}$)

When preparing calibration solutions, use a volumetric flask and a micropipette. If the uncertainty is dependent on the concentration, use the uncertainty at the concentration where it is the greatest. In this case, $u_{3.4.2}$ is determined by combining the relative standard uncertainties of the volumetric flask ($u_{3.4.2.a}$) and micropipette ($u_{3.4.2.b}$).

4-3) Combination of uncertainties ($u_{3.4}$)

Combine $u_{3.4.1}$ and $u_{3.4.2}$ to obtain $u_{3.4}$:

$$u_{3.4} = \sqrt{(u_{3.4.1})^2 + (u_{3.4.2})^2} \quad \text{(A.27)}$$

[Calculation Example]

This example shows how to obtain $u_{3.4.2}$ when preparing a 0.1 µg/L $^{127}$I calibration solution by diluting a 10,000 mg/L calibration solution (Table I.A.3).

Table I.A.3 Dilution method for calibration solutions

| | Predilution concentration | Micropipette used | Measuring flask used | Concentration after dilution |
|---|---|---|---|---|
| 1 | 10000 mg/L | 0.1 mL | 100 mL | 10 mg/L |
| 2 | 10 mg/L | 1.0 mL | 100 mL | 0.1 mg/L |
| 3 | 0.1 mg/L | 0.1 mL | 100 mL | 0.1 µg/L |

In this case, a 100 mL volumetric flask and two micropipettes (0.1 mL and 1.0 mL) are used. Hence, $u_{3.4.2}$ is obtained by combining the relative standard uncertainties of the 100 mL volumetric flask ($u_{3.4.2.a}$), 0.1 mL micropipette ($u_{3.4.2.b}$), and 1.0 mL micropipette ($u_{3.4.2.c}$).

a) Uncertainty of the volumetric flask ($u_{3.4.2.a}$)

Determine the uncertainty of the capacity of the 100 mL volumetric flask with a tolerance of 0.1 mL ($u_{3.4.2.a1}$) using Equation (A.15) as follows:

$$u_{3.4.2.a1} = \frac{V_i}{\sqrt{3} \times V} \times 100 = \frac{0.1}{\sqrt{3} \times 100} \times 100 = 0.058\ \%$$

When the mean of repeated measurements is 100.002 g, standard deviation is 0.059 g, and number of measurements per sample is 1, the uncertainty due to the repeatability of the volumetric flask ($u_{3.4.2.a2}$) is determined using Equation (A.16) as follows:

$$u_{3.4.2.a2} = \frac{W_{STD}}{W} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.059}{100.002} \times \frac{1}{\sqrt{1}} \times 100 = 0.059\ \%$$

Combine $u_{3.4.2.a1}$ and $u_{3.4.2.a2}$ to obtain $u_{3.4.2.a}$:

$$u_{3.4.2.a} = \sqrt{(u_{3.4.2.a1})^2 + (u_{3.4.2.a2})^2} = \sqrt{(0.058)^2 + (0.059)^2} = 0.083\ \%$$

b) Uncertainty of the micropipette ($u_{3.4.2.b}$ and $u_{3.4.2.c}$)

First, obtain $u_{3.4.2.b}$. The calibration uncertainty of the micropipette ($u_{3.4.2.b1}$) is obtained from Equation (A.18) as follows when the calibration value stated on the calibration certificate of the micropipette is 1000.0 $\mu$L, expanded uncertainty at calibration is 0.8 $\mu$L, and coverage factor is 2:

$$u_{3.4.2.b1} = \frac{U_{pipette}/k}{V_{pipette}} \times 100 = \frac{0.8/2}{1000.0} \times 100 = 0.040\ \%$$

When the mean of repeated measurements is 0.9974 g, standard deviation is 0.0017 g, and number of measurements per sample is 1, the uncertainty due to the repeatability ($u_{3.4.2.b2}$) is determined using Equation (A.20) as follows:

$$u_{3.4.2.b2} = \frac{W_{STD}}{W} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.0017}{0.9974} \times \frac{1}{\sqrt{1}} \times 100 = 0.17\,\%$$

Next, combine $u_{3.4.2.b1}$ and $u_{3.4.2.b2}$ to obtain $u_{3.4.2.b}$:

$$u_{3.4.2.b} = \sqrt{(u_{3.4.2.b1})^2 + (u_{3.4.2.b2})^2} = \sqrt{0.040^2 + 0.17^2} = 0.17\,\%$$

Further, obtain $u_{3.4.2.c}$. When using a 0.1 mL micropipette with a tolerance of 0.001 mL, the uncertainty pertaining to volume ($u_{3.4.2.c1}$) is determined from Equation (A.19) as follows:

$$u_{3.4.2.c1} = \frac{V_{i\,pipette}}{\sqrt{3} \times V_{pipette}} \times 100 = \frac{0.001}{\sqrt{3} \times 0.1} \times 100 = 0.58\,\%$$

When the mean of repeated measurements is 0.10008 g, standard deviation is 0.000070 g, and number of measurements per sample is 1, the uncertainty due to repeatability ($u_{4.4.2.c2}$) is determined using Equation (A.20) as follows:

$$u_{3.4.2.c2} = \frac{W_{STD}}{W} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.000070}{0.10008} \times \frac{1}{\sqrt{1}} \times 100 = 0.070\,\%$$

Combine $u_{3.4.2.c1}$ and $u_{3.4.2.c2}$ to obtain $u_{3.4.2.c}$:

$$u_{3.4.2.c} = \sqrt{(u_{3.4.2.c1})^2 + (u_{3.4.2.c2})^2} = \sqrt{0.58^2 + 0.070^2} = 0.58\,\%$$

c) Combination of uncertainties ($u_{3.4.2}$ and $u_{3.4}$)

Combine $u_{3.4.2.a}$–$u_{3.4.2.c}$ to obtain $u_{3.4.2}$:

$$u_{3.4.2} = \sqrt{(u_{3.4.2.a})^2 + (u_{3.4.2.b})^2 + (u_{3.4.2.c})^2} = \sqrt{0.083^2 + 0.17^2 + 0.58^2} = 0.61\,\%$$

Next, combine $u_{3.4.1}$ and $u_{3.4.2}$ to obtain $u_{3.4}$:

$$u_{3.4} = \sqrt{(u_{3.4.1})^2 + (u_{3.4.2})^2} = \sqrt{0.068^2 + 0.61^2} = 0.61\,\%$$

5) Combination of uncertainty ($u_3$)

Combine $u_{3.1}$–$u_{3.4}$ to obtain $u_3$:

$$u_3 = \sqrt{(u_{3.1})^2 + (u_{3.2})^2 + (u_{3.3})^2 + (u_{3.4})^2} \quad \text{(A.28)}$$

[Calculation Example]

Using Equation (A.28), $u_3$ is obtained by combining $u_{3.1}$–$u_{3.4}$ as follows:

$$u_3 = \sqrt{(u_{3.1})^2 + (u_{3.2})^2 + (u_{3.3})^2 + (u_{3.4})^2}$$
$$= \sqrt{0.0090^2 + 0.18^2 + 1.3^2 + 0.61^2} = 1.4\,\%$$

(4) Uncertainty in the weighing of palladium iodide ($u_4$)

Perform the same calculation as in "b) When the calibration certificate does not include uncertainty information" in "(1) Uncertainty of weighing" in "A.3.1 Uncertainty of the Sample Quantity." $u_4$ is obtained by combining the relative standard uncertainties pertaining to the rounding of the weighed amount ($u_{4.1}$) and repeatability ($u_{4.2}$).

[Calculation Example]

When using an electronic balance with a readability of 0.1 mg and the weighed amount is

30.06 mg, $u_{4.1}$ is obtained from Equation (A.8) as follows:

$$u_{4.1} = \frac{l}{\sqrt{6} \times W} \times 100 = \frac{0.1}{\sqrt{6} \times 30.06} \times 100 = 0.14\,\%$$

When the mean of repeated measurements is 29.745 mg, standard deviation is 0.141 mg, and number of measurements per sample is 1, $u_{4.2}$ is obtained from Equation (A.9) as follows:

$$u_{4.2} = \frac{W_{\mathrm{STD}}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.141}{29.745} \times \frac{1}{\sqrt{1}} \times 100 = 0.47\,\%$$

Then, $u_{4.1}$ and $u_{4.2}$ are combined to obtain $u_4$:

$$u_4 = \sqrt{(u_{4.1})^2 + (u_{4.2})^2} = \sqrt{0.14^2 + 0.47^2} = 0.49\,\%$$

(5) Calculation of the relative composite standard uncertainty of $Z$

As mentioned earlier, to obtain $\frac{u(Z)}{Z}$, it is necessary to calculate $u(Z)$. For this, first multiply $u_2$, $u_3$, and $u_4$ by their respective input values to obtain $u(W_1)$, $u(C_\mathrm{I})$, and $u(W\mathrm{s})$. Next, after calculating $u(Z)$ using Equation (A.13), $\frac{u(Z)}{Z}$ is obtained.

[Calculation Example]

Based on (2)–(4), $u_2$, $u_3$, and $u_4$ are obtained as follows:

$$u_2 = \frac{u(W_1)}{W_1} = 0.18\,\% = 0.0018$$

$$u_3 = \frac{u(C_\mathrm{I})}{C_\mathrm{I}} = 1.4\,\% = 0.014$$

$$u_4 = \frac{u(W_\mathrm{s})}{W_\mathrm{s}} = 0.49\,\% = 0.0049$$

First, the standard uncertainty is calculated from individual relative standard uncertainties. For this calculation example, consider the previously specified analysis conditions: $W_1$ = 20 mg, $C_\mathrm{I}$ = 0.65 mg/g, and $W\mathrm{s}$ = 0.50 g.

$$u(W_1) = W_1 \times u_2 = W_1 \times \frac{u(W_1)}{W_1} = 20\ \mathrm{mg} \times 0.0018 = 0.036\ \mathrm{mg}$$

$$u(C_\mathrm{I}) = C_\mathrm{I} \times u_3 = C_\mathrm{I} \times \frac{u(C_\mathrm{I})}{C_\mathrm{I}} = 0.65\ \mathrm{mg/g} \times 0.014 = 0.0091\ \mathrm{mg/g}$$

$$u(W_\mathrm{s}) = W_\mathrm{s} \times u_4 = W_\mathrm{s} \times \frac{u(W_\mathrm{s})}{W_\mathrm{s}} = 0.50\ \mathrm{g} \times 0.0049 = 0.0025\ \mathrm{g}$$

Next, $u(Z)$ is obtained from Equation (A.13) as follows:

$$u(Z) = \sqrt{\left(u(W_1)\right)^2 + {W_\mathrm{s}}^2 \times (u(C_\mathrm{I}))^2 + {C_\mathrm{I}}^2 \times \left(u(W_\mathrm{s})\right)^2}$$

$$= \sqrt{0.036^2 + 0.50^2 \times 0.0091^2 + 0.65^2 \times 0.0025^2} = 0.036\ \mathrm{mg}$$

Lastly, $Z$ = 20.3 mg is used to determine $\frac{u(Z)}{Z}$:

$$\frac{u(Z)}{Z} = \frac{0.036}{20.3} \times 100 = 0.18\,\%$$

(6) Uncertainty in the amount of $^{127}$I determined by recovery rate measurements ($u_5$)

The recovery rate for the measurement target nuclide $^{129}$I is assumed to be identical to that of $^{127}$I, and the analysis is carried out under the assumption that there are no deviations due to systematic or random effects. The recovery rate in $^{127}$I analysis is determined by comparing the total amount of $^{127}$I added as the carrier with the amount of $^{127}$I in palladium iodide. The uncertainty ($u_5$) of the $^{127}$I quantity determined by recovery rate measurements is derived from the uncertainty of the weighed amount of palladium iodide in the measurement sample.

[Calculation Example]

When weighing palladium iodide (weighed amount = 30.06 mg) using an electronic balance with a readability of 0.1 mg, the uncertainty of weighing ($u_{5.1}$) is determined using Equation (A.8) as follows:

$$u_{5.1} = \frac{l}{\sqrt{6} \times W} \times 100 = \frac{0.1}{\sqrt{6} \times 30.06} \times 100 = 0.14\,\%$$

When the mean of repeated measurements is 29.745 mg, standard deviation is 0.141 mg, and number of measurements per sample is 1, the uncertainty pertaining to the repeatability of weighing ($u_{5.2}$) is determined using Equation (A.9) as follows:

$$u_{5.2} = \frac{W_{STD}}{W} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.141}{29.745} \times \frac{1}{\sqrt{1}} \times 100 = 0.47\,\%$$

Then, $u_{5.1}$ and $u_{5.2}$ are combined to obtain $u_5$:

$$u_5 = \sqrt{(u_{5.1})^2 + (u_{5.2})^2} = \sqrt{0.14^2 + 0.47^2} = 0.49\,\%$$

(7) Combination of uncertainties of the recovery rate value $Y$ $\left(\frac{u(Y)}{Y}\right)$

Combine $\frac{u(Z)}{Z}$ and $u_5$(= $\frac{u(W_2)}{W_2}$ )obtained in (5) and (6) using Equation (A.12) to determine $\left(\frac{u(Y)}{Y}\right)$.

[Calculation Example]

The values of $\frac{u(Z)}{Z}$ and $\frac{u(W_2)}{W_2}$ obtained in (5) and (6) are as follows:

$$\frac{u(Z)}{Z} = 0.18\,\%$$

$$\frac{u(W_2)}{W_2} = 0.49\,\%$$

From Equation (A.12), $\frac{u(Y)}{Y}$ is obtained as follows:

$$\frac{u(Y)}{Y} = \sqrt{\left(\frac{u(Z)}{Z}\right)^2 + \left(\frac{u(W_2)}{W_2}\right)^2} = \sqrt{0.18^2 + 0.49^2} = 0.52\,\%$$

### A.3.3 Uncertainty in the Counting Efficiency $\varepsilon$ of $^{129}$I $\left(\frac{u(\varepsilon)}{\varepsilon}\right)$

The counting efficiency $\varepsilon$ of a detector is determined by measuring a sample prepared using a $^{129}$I standard solution for generating a counting efficiency curve. The equation for calculating the counting efficiency in $^{129}$I measurements is as follows:

$$\varepsilon = \frac{r_{std} \times 100}{B \times Y} \quad \text{A.29}$$

$\varepsilon$ : Counting efficiency (cps/Bq)

$r_{std}$ : Net counting rate (cps) of the sample used for generating the counting efficiency curve

$B$ : Amount of added $^{129}$I (Bq)

$Y$ : Recovery rate (%)

From Equation (A.29), factors that could contribute to uncertainty are extracted as follows: from $B$, (1) the standard solution and (2) the aliquoting of the standard solution; from $r_{std}$, (3) the measurement of the sample for generating the calibration curve and (4) the recovery rate of the sample used for generating the calibration curve. By synthesizing the relative standard uncertainty for these factors, the uncertainty in the counting efficiency $\left(\frac{u(\varepsilon_S)}{\varepsilon_S}\right)$ is determined.

(1) Uncertainty of the standard solution ($u_6$)

Use the expanded uncertainty stated in the standard solution's certificate to determine $u_6$.

$$u_6 = \frac{U_{std}}{k} \ (\%) \quad \text{(A.30)}$$

$U_{std}$: Expanded uncertainty of the standard solution (%)

$k$ : Coverage factor

[Calculation Example]

When expanded uncertainty of a $^{129}$I standard solution is 6.0% and the coverage factor is 2, the standard uncertainty $u_6$ is determined using Equation (A.30) as follows:

$$u_6 = \frac{U_{std}}{k} = \frac{6.0}{2} = 3.0\,\%$$

(2) Uncertainty due to aliquoting of the standard solution ($u_7$)

As with $u_3$, uncertainty in this case is determined by combining the relative standard uncertainties of pipette calibration ($u_{7.1}$) and repeatability ($u_{7.2}$).

[Calculation Example]

When the calibration value of the 5 mL micropipette used to add the standard solution is 5014.5 $\mu$L, expanded uncertainty of calibration is 2.8 $\mu$L, and coverage factor is 2, $u_{7.1}$ is obtained using Equation (A.18) as follows:

$$u_{7.1} = \frac{U_{pipette}/_{k}}{V_{pipette}} \times 100 = \frac{2.8/2}{5014.5} \times 100 = 0.028\,\%$$

When the mean of repeated measurements is 5.0018 g, standard deviation is 0.0034 g, and number of measurements per sample is 1, the uncertainty due to repeatability ($u_{7.2.2}$) is determined using Equation (A.20) as follows:

$$u_{7.2} = \frac{W_{\mathrm{STD}}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.0034}{5.0018} \times \frac{1}{\sqrt{1}} \times 100 = 0.068\,\%$$

Then, $u_{7.1}$ and $u_{7.2}$ are combined to determine the uncertainty ($u_7$) due to the aliquoting of the standard solution:

$$u_7 = \sqrt{(u_{7.1})^2 + (u_{7.2})^2}$$
$$= \sqrt{0.028^2 + 0.068^2} = 0.074\,\%$$

(3) Uncertainty resulting from the measurement of samples for generating the efficiency curve ($u_8$)

Calculate the relative standard uncertainty based on the counting rate of samples used for generating the efficiency curve and the uncertainty associated with counting statistics.

$$u_8 = \frac{\sigma_{\mathrm{std}}}{r_{\mathrm{std}}} \times 100(\%) \qquad \text{(A.31)}$$

$r_{\mathrm{std}}$ : Counting rate of samples used for generating efficiency curves

$\sigma_{\mathrm{std}}$ : Uncertainty of counting statistics

[Calculation Example]

Assume that a sample is prepared from the standard solution and measured for generating an efficiency curve (counting rate = 13.117 and statistical uncertainty of the count = 0.061). Then, $u_8$ is obtained from Equation (A.31) as follows:

$$u_8 = \frac{0.061}{13.117} \times 100 = 0.47\,\%$$

(4) Uncertainty in the recovery rates of samples used for generating efficiency curves ($u_9$)

The recovery rate of the sample used for generating the efficiency curve is obtained from Equation

$$Y = \frac{W_p \times R}{W_1} \times 100\ (\%) \qquad \text{(A.32)}$$

$Y$ : Recovery rate (%)

$W_1$ : Amount of $^{127}$I added as a carrier (mg)

$W_p$ : Weight of precipitated palladium iodide (mg)

$R$ : Weight ratio of $^{127}$I in palladium iodide (0.7046)

From Equation (A.32), the following factors that could contribute to uncertainty in the recovery rate of the sample used for generating the efficiency curve are identified: 1) the weighing of palladium iodide and 2) amount of iodine in the added standard solution. Therefore, the uncertainties of these factors are combined to obtain $u_9$.

1) Uncertainty due to the weighing of palladium iodide ($u_{9.1}$)

   Perform the same calculation as in "A.3.1 Uncertainty of the Sample Quantity."

2) Uncertainty due to the aliquoting of the standard solution ($u_{9.2}$)

   Perform the same calculation as in "(2) Uncertainty in the amount of $^{127}$I added as the carrier" in "A.3.2 Uncertainty of the Recovery Rate."

(5) Combination of uncertainties in the counting efficiency $\varepsilon$ $(\frac{u(\varepsilon)}{\varepsilon})$

Combine $u_6$–$u_9$ to obtain $\frac{u(\varepsilon)}{\varepsilon}$:

$$\frac{u(\varepsilon)}{\varepsilon} = \sqrt{(u_6)^2 + (u_7)^2 + (u_8)^2 + (u_9)^2} \quad \text{(A.33)}$$

[Calculation Example]

When weighing palladium iodide, the uncertainty ($u_{9.1.1}$) in rounding the weighed amount of 30.2 mg on an electronic balance with a readability of 0.1 mg is obtained from Equation (A.8) as follows:

$$u_{9.1.1} = \frac{l}{\sqrt{6} \times W} \times 100 = \frac{0.1}{\sqrt{6} \times 30.2} \times 100 = 0.14\,\%$$

When the mean of repeated measurements is 29.7 mg, standard deviation is 0.1 mg, and number of measurements per sample is 1, the uncertainty due to the repeatability of weighing ($u_{9.1.2}$) is determined using Equation (A.9) as follows:

$$u_{9.1.2} = \frac{W_{STD}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.1}{29.7} \times \frac{1}{\sqrt{1}} \times 100 = 0.34\,\%$$

Then, $u_{9.1}$ is obtained from Equation (A.10) as follows:

$$u_{9.1} = \sqrt{(u_{9.1.1})^2 + (u_{9.1.2})^2} = \sqrt{0.14^2 + 0.34^2} = 0.37\,\%$$

When the micropipette's calibration value is 5014.5 $\mu$L, expanded uncertainty of calibration is 2.8 $\mu$L, and coverage factor is 2, the calibration uncertainty ($u_{9.2.1}$) is obtained from Equation (A.18) as follows:

$$u_{9.2.1} = \frac{U_{pipette}/k}{V_{pipette}} \times 100 = \frac{2.8/2}{5014.5} \times 100 = 0.028\,\%$$

When the mean of repeated measurements is 5.0018 g, standard deviation is 0.0034 g, and number of measurements per sample is 1, the uncertainty due to repeatability ($u_{9.2.2}$) is determined using Equation (A.20) as follows:

$$u_{9.2.2} = \frac{W_{STD}}{\overline{W}} \times \frac{1}{\sqrt{n}} \times 100 = \frac{0.0034}{5.0018} \times \frac{1}{\sqrt{1}} \times 100 = 0.068\,\%$$

Then, $u_{9.2}$ is obtained from Equation (A.21):

$$u_{9.2} = \sqrt{(u_{9.2.1})^2 + (u_{9.2.2})^2} = \sqrt{0.028^2 + 0.068^2} = 0.074\,\%$$

Further, $u_{9.1}$ and $u_{9.2}$ are combined to obtain the uncertainty in the recovery rate of the sample used for generating the efficiency curve ($u9$):

$$u_9 = \sqrt{(u_{9.1})^2 + (u_{9.2})^2} = \sqrt{0.37^2 + 0.074^2} = 0.38\,\%$$

The uncertainty in the counting efficiency ($\frac{u(\varepsilon)}{\varepsilon}$) is obtained from Equation (A.33) as follows:

$$\frac{u(\varepsilon)}{\varepsilon} = \sqrt{(u_6)^2 + (u_7)^2 + (u_8)^2 + (u_9)^2}$$
$$= \sqrt{3.0^2 + 0.074^2 + 0.47^2 + 0.38^2} = 3.1\,\%$$

### A.3.4 Uncertainty in the Net Counting Rate $r_n$ of $^{129}$I ($\frac{u(r_n)}{r_n}$)

In $^{129}$I measurements, the radioactivity concentration is calculated by applying detector counting efficiency and recovery rate corrections to the net counting rate, which is obtained by subtracting the background counting rate from the measured sample counting rate. Therefore, ($\frac{u(r_n)}{r_n}$) is determined by combining the relative standard uncertainties of statistical counting ($u_{10}$) and measurement system variability ($u_{11}$).

(1) Uncertainty in counting statistics ($u_{10}$)

Calculate the relative standard uncertainty based on the counting rate and the statistical uncertainty of the count obtained from the measurement of an unknown sample.

$$u_{10} = \frac{\sigma_{r_n}}{r_n} \times 100\ (\%) \qquad \text{(A.34)}$$

$rn$ : Net counting rate of the unknown sample

$\sigma rn$ : Uncertainty in counting statistics

[Calculation Example]

Assume a sample measurement time of 60 minutes, an unknown-sample count value of 1500 counts, and a background count value of 8 counts. In this case, the statistical uncertainty $u_{10}$ of the counting rate of 0.4144 ± 0.0108 cps is obtained from Equation (A.34) as follows:

$$u_{10} = \frac{\sigma_{r_n}}{r_n} \times 100 = \frac{0.0108}{0.4144} \times 100 = 2.6\,\%$$

(2) Uncertainty due to fluctuations in the measurement system ($u_{11}$)

The uncertainty due to fluctuations in the measurement system can be estimated by determining the stability of the measuring instrument, specifically the tolerance limits for the fluctuation range.

For example, as a part of routine precision control, when measuring a radioactive check source under specified conditions, a tolerance range of ±R can be established for fluctuations. This tolerance may be defined as the difference between the obtained counting rate and the value specified on the performance certificate that lies within a certain range or as the difference

between the obtained counting rate and the mean value for the radioactive check source over the past year that is within three times the standard deviation. This tolerance range ±R can then be used in the calculation of uncertainty.

Since $u_{11}$ is assumed to follow a rectangular distribution, with the tolerance limits defining the upper and lower bounds, it is calculated using the following equation:

$$u_{11} = \frac{R}{\sqrt{3}} \times 100(\%) \quad \text{(A.35)}$$

$R$ : Upper bound of the tolerance limit for fluctuations

(3) Combination of uncertainties in the net counting rate of $^{129}$I $\left(\frac{u(r_n)}{r_n}\right)$ are combined to obtain.

$u_{10}$ and $u_{11}$ are combined to obtain $\frac{u(r_n)}{r_n}$

$$\frac{u(r_n)}{r_n} = \sqrt{(u_{10})^2 + (u_{11})^2} \quad \text{(A.36)}$$

[Calculation Example]

When the tolerance limit determined by measuring a radioactive check source is ±0.6%, $u_{11}$ can be determined from Equation (A.35) as follows:

$$u_{11} = \frac{R}{\sqrt{3}} \times 100 = \frac{0.006}{\sqrt{3}} \times 100 = 0.35\ \%$$

The uncertainty in the sample measurement $\left(\frac{u(r_n)}{r_n}\right)$ is obtained from Equation (A.36) as follows:

$$\frac{u(r_n)}{r_n} = \sqrt{(u_{10})^2 + (u_{11})^2} = \sqrt{2.6^2 + 0.35^2} = 2.6\ \%$$

### A.3.5 Uncertainty in the Radioactivity Concentration $A$ of $^{129}$I $\left(\frac{u(A)}{A}\right)$

Using Equation (A.6), combine the relative standard uncertainties obtained in A.3.1–A.3.4 to obtain $u(A)$.

[Calculation Example]

The relative standard uncertainties determined in A.3.1–A.3.4 are as follows.

$$\frac{u(W_s)}{W_s} = 0.011\ \%$$

$$\frac{u(Y)}{Y} = 0.52\ \%$$

$$\frac{u(\varepsilon)}{\varepsilon} = 3.1\%$$

$$\frac{u(r_n)}{r_n} = 2.6\ \%$$

Then, $\frac{u(A)}{A}$ is obtained using Equation (A.6) as follows:

$$\frac{u(A)}{A} = \sqrt{\left(\frac{u(W_s)}{W_s}\right)^2 + \left(\frac{u(Y)}{Y}\right)^2 + \left(\frac{u(\varepsilon)}{\varepsilon}\right)^2 + \left(\frac{u(r_n)}{r_n}\right)^2}$$

$$= \sqrt{0.011^2 + 0.52^2 + 3.1^2 + 2.6^2} = 4.1\,\%$$

In this calculation example, the uncertainty factors that contributed most significantly to the overall uncertainty were the uncertainty associated with the standard solution and the uncertainty arising from statistical counting. In the measurement of environmental samples, $^{129}$I is often detected at low concentrations, and the contribution of uncertainty arising from statistical counting is frequently significant. Hence, it is recommended to compare the contributions of each uncertainty factor. For factors with a significant impact, evaluate whether modifying the analysis and measurement conditions can reduce the uncertainty. In this example, the uncertainty contribution associated with the standard solution is the largest. Since the uncertainty of standard solutions is expected to vary depending on the manufacturer, production method, and production lot, it is advisable to calculate and evaluate the uncertainty before purchasing updated standard solutions. The calculation examples provided for iodine measurement include factors with small contributions to help master evaluation techniques for various factors. However, when actually performing uncertainty evaluation, it is advisable to prioritize the evaluation of the uncertainty associated with the standard solution and the uncertainty arising from statistical counting. Moreover, to reliably evaluate uncertainty factors with significant contributions, it is advisable to refer to the uncertainties of each factor in this calculation example, assess additional factors likely to introduce large uncertainties, combine them with the statistical uncertainty of the measurements, and then determine whether these uncertainty factors should be considered.

# Explanation B : Example of Calculating the Lower Detection Limit

## B.1 Lower Detection Limit According to ISO 11929

### B.1.1 Concept

ISO 11929 defines the lower detection limit and decision threshold by introducing the concepts of Type-I error and Type-II error for the distributions of background values and measured values, respectively[*157].

Furthermore, it allows for the inclusion of uncertainty in the standard deviation of each distribution. In Kaiser's method, the standard deviation of the distribution of measured values is based on the uncertainty associated with the count. However, for the lower detection limit according to ISO 11929, the standard deviation of the distribution is based on the combined standard uncertainty of the measured values as per the "Guide to the Expression of Uncertainty in Measurement" (GUM)[*158].

### B.1.2 Decision Threshold ($A^*$)

Decision threshold is a value that determines the presence of physical effects. It is defined by the distribution of blank measurements and expressed as follows:

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

$A^*$ : Decision threshold

$k_{1-\alpha}$ : Coefficient with a confidence level of $1 - \alpha$

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

In the measurements of backgrounds that contain absolutely no radioactive nuclides to be measured, the measured values follow the distribution shown in Figure I.B.1 ($\mu = 0$). In this distribution, the upper limit of the interval corresponding to a confidence level of $1 - \alpha$ is set as the decision threshold. Measurements exceeding this upper limit are determined to be Type-I errors, indicating a significant deviation from the blank and the presence of physical effects. Here, the probability of a Type-I error is $\alpha$.

[*157] ISO 11929-1:2019: Determination of the characteristic limits (decision threshold, detection limit and limits of the coverage interval) for measurements of ionizing radiation — Fundamentals and application Part 1: Elementary applications (2019)

[*158] 今井秀孝 他 著: 日本規格協会出版、2018 年6 月27 日発行, ISBN: 9784542307056

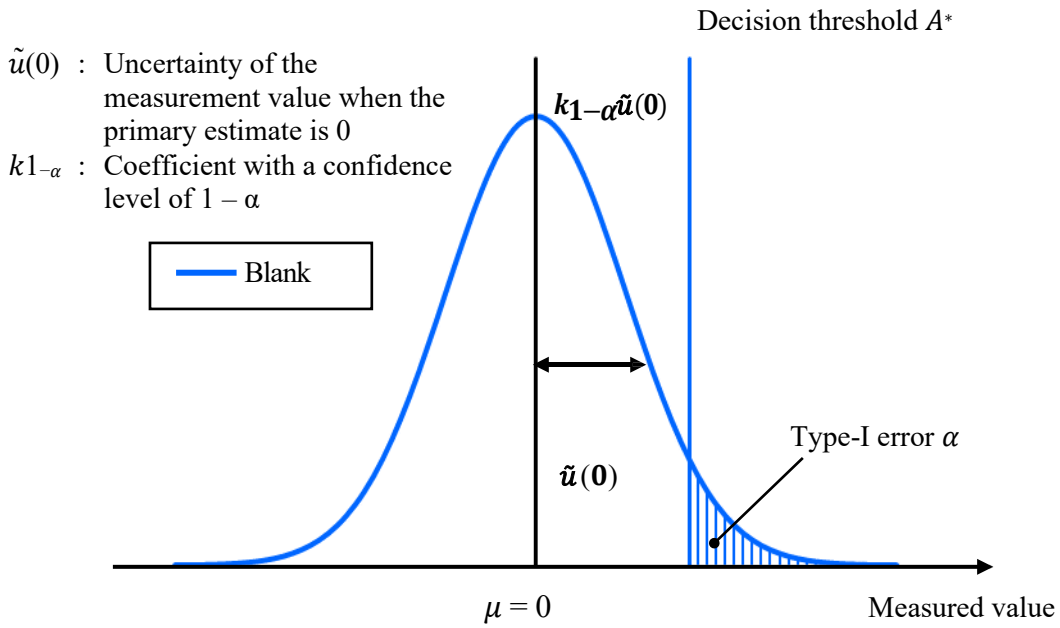



Figure I.B.1 Decision threshold

### B.1.3 Lower Detection Limit ($A^{\#}$)

The lower limit of detection represents the contribution from the sample rather than solely from the blank. It is defined as follows:

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

$A^{\#}$ : Lower detection limit
$k_{1-\beta}$ : Coefficient with a power of $1 - \beta$
$\tilde{u}(A^{\#})$ : 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 but close to the decision threshold, the distribution of the measured values resembles that shown in Figure I.B.2 and overlaps with the distribution of blank measurements.

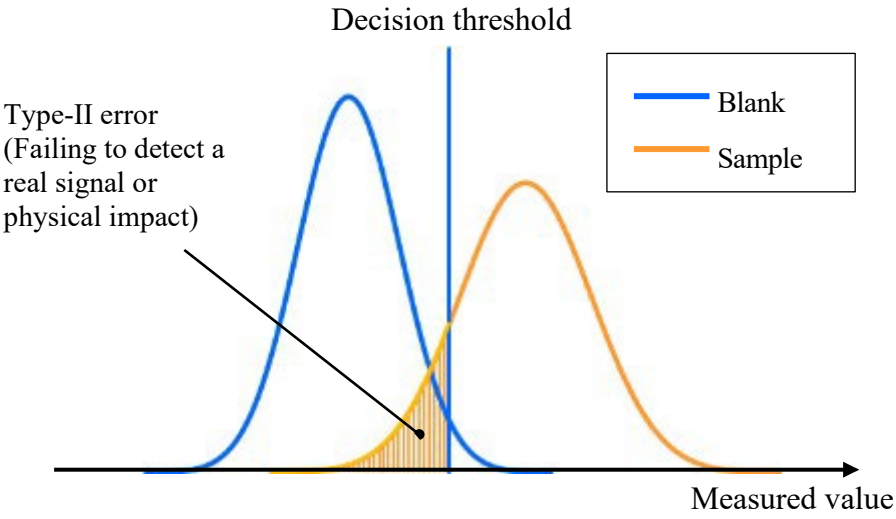



Figure I.B.2 Distribution of measured values when the primary estimate is close to the decision threshold

The measured values in the section indicated in red in Figure I.B.3 fall below the determination threshold. Hence, it is judged that no physical effects exists. Therefore, in the distribution of sample measurements, an interval with a power of 1 − α is established. As shown in Figure I.B.3, when the lower limit of this interval coincides with the decision threshold, the primary estimate of the measurement value is set as the detection limit. Then, the probability of a Type-II error is $\beta$.

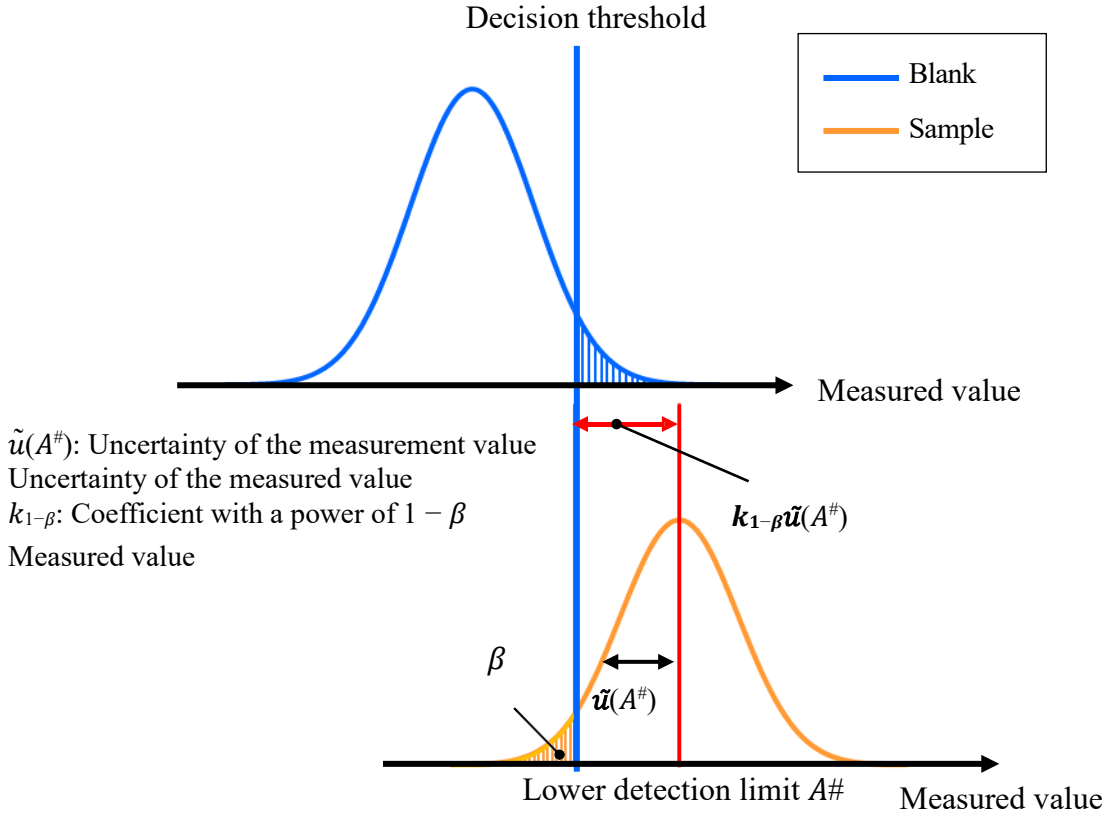



Figure I.B.3 Lower detection limit

The lower detection limit is used to evaluate the measurement procedure through comparison with the guideline value $Ar$. When $A^{\#} < A_r$, the measurement procedure is evaluated as appropriate.

When $A_r$, it is necessary to reduce the detection limit by extending the measurement time or revising the count. ISO 11929-4:2022 specifies a guideline value $A_r$ of 3 Bq for general measurements. (For cases where the background count is low, it is set to 0.1 Bq.)

Here, the guideline value $A_r$ according to ISO 11929-1:2019 is the value that meets scientific, legal, or other requirements concerning detection capability and further serves as a value for evaluating the measurement procedure by comparison with the lower detection limit.

Note 1: Guideline values of radioactivity, specific activity, radioactivity concentration, radioactivity surface density, and dose rate are generally provided.

Note 2: By comparing the detection limit with the guideline value, it is possible to determine whether the measurement procedure meets the requirements specified by the guideline value. Thus, it is possible to determine whether it is suitable for the intended measurement purpose. The measurement procedure meets the requirements when the detection limit is lower than the guideline value.

Note 3: Do not mix guideline values with other values specified in conformity requirements or regulatory limits.

Figure I.B.4 summarizes the concepts of the decision threshold and detection limit in a single figure.

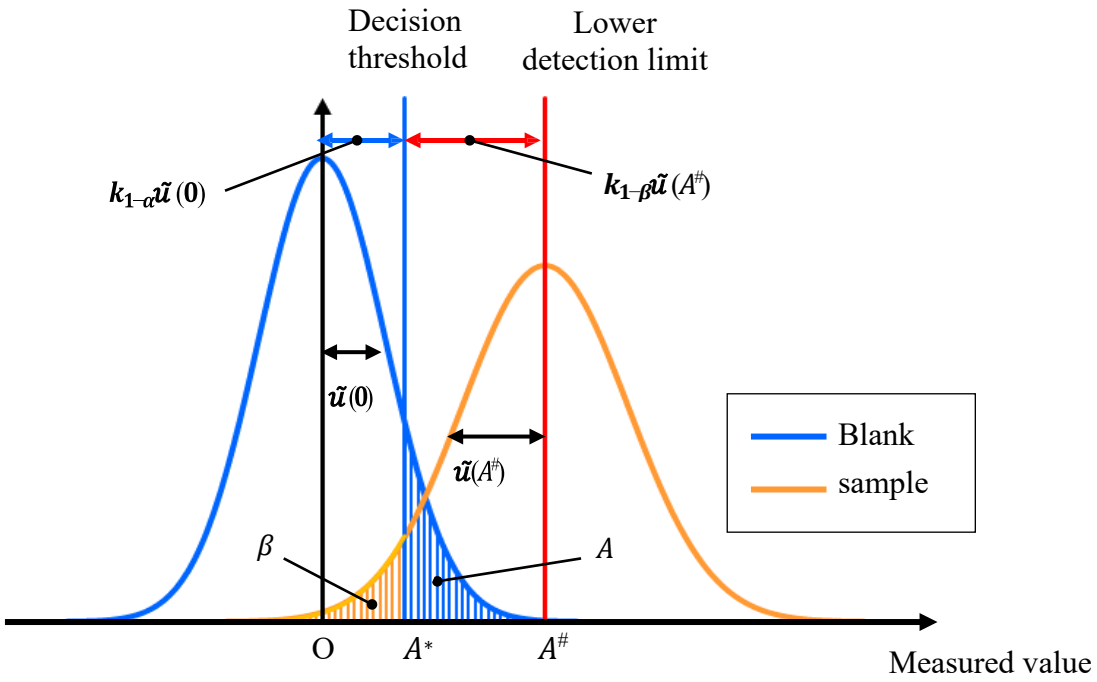



Figure I.B.4 Concept of the lower detection limit according to ISO 11929

### B.1.4 Example of Calculating the Lower Detection Limit According to ISO 11929

Using the model equation specified in ISO 11929-4[*159], the decision threshold and lower detection limit can be determined as follows.

(1) General formula for determining radioactivity from measured values

$$A = r_n \times w = (r_s - r_0) \times w \tag{B.3}$$

$A$ : Measured value (radioactivity concentration)

$r_n$ : Net counting rate

$w$ : Conversion factor from the counting rate to radioactivity. When detection efficiency is denoted by $\varepsilon$, chemical recovery rate by $Y$, sample quantity (kg, L, etc.) by $W_s$, and decay correction factor by $DF$, holds true.

$$w = \frac{1}{\varepsilon \times Y \times W_s \times DF}$$

However, when determining the radioactivity concentration $A$, $W_s$ is not required.

$r_s$ : Counting rate of sample measurement. When the number of sample measurements is set as $N_s$ and the measurement time as $t_s$, then $r_s = N_s/t_s$ holds true.

$r_0$ : Counting rate of background measurements. When the background measurement count is set as $N_0$ and the measurement time as $t_0$, then $r_0 = N_0/t_0$ holds true.

When the uncertainties of $r_n$ and $w$ are denoted as $u(r_n)$ and $u(w)$, respectively, the uncertainty $u(A)$ of $A$ is expressed as follows:

$$u(A) = r_n \times w \times \sqrt{\left(\frac{u(r_n)}{r_n}\right)^2 + \left(\frac{u(w)}{w}\right)^2} \tag{B.4}$$

$$= \sqrt{w^2\, u^2(r_n) + r_n^2\, u^2(w)} \tag{B.5}$$

Furthermore, substituting $r_n = A/w$ and $u(r_n) = \sqrt{r_s/t_s + r_0/t_0}$ into (B.5) yields the following expression:

$$u(A) = \sqrt{w^2 \left(\frac{r_s}{t_s} + \frac{r_0}{t_0}\right) + A^2 \frac{u^2(w)}{w^2}} \tag{B.6}$$

$u^2(w)/w^2$ represents the relative standard uncertainty $u_{rel}(w)$, excluding the uncertainty pertaining to measurement counting.

To calculate the decision threshold and lower detection limit as per ISO 11929, a function of the measurement uncertainty $\tilde{u}(\tilde{A})$ is required, where the variable is the primary estimate $\tilde{A}$ of the measured value. From Equation (B.3), the following expression is obtained using the

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

primary estimate $\tilde{A}$:

$$r_s = \frac{\tilde{A}}{w} + r_b \tag{B.7}$$

Substituting this into Equation (B.6) yields the following expression:

$$\tilde{u}(\tilde{A}) = \sqrt{w^2 \left( \frac{\left( \frac{\tilde{A}}{w} + r_0 \right)}{t_s} + \frac{r_0}{t_0} \right) + \tilde{A}^2 \frac{u^2(w)}{w^2}} \tag{B.8}$$

(2) Decision threshold

Substitute the primary estimate of the measurement value $\tilde{A} = 0$ into Equation (B.8). Then, substitute the obtained expression in $\tilde{u}(0)$ in Equation (B.1).

$$A^* = k_{1-\alpha}\, w \sqrt{\frac{N_0}{t_0 \times t_s} + \frac{N_0}{{t_0}^2}} \tag{B.9}$$

$A^*$ : Decision threshold (Bq or Bq/kg, Bq/L, etc.)

$k_{1-\alpha}$ : Coefficient for preventing Type-I errors (i.e., errors arising from concluding that an effect or signal exists when it does not)

(3) Lower detection limit

When the detection limit is set to $A^{\#}$, substitute $A^{\#}$ into Equation (B.8) and then substitute the resulting expression in $\tilde{u}(A^{\#})$ in Equation (B.2).

$$\begin{aligned}
A^{\#} &= A^* + k_{1-\beta} \sqrt{w^2 \left( \left( \frac{A^{\#}}{w} + r_0 \right) / t_s + \frac{r_0}{t_0} \right) + A^{\#2} \frac{u^2(w)}{w^2}} \\
(A^{\#} - A^*)^2 &= k_{1-\beta}^2 \left[ w^2 \left( \left( \frac{A^{\#}}{w} + r_0 \right) / t_s + \frac{r_0}{t_0} \right) + A^{\#2} \frac{u^2(w)}{w^2} \right] \\
\left( 1 - k_{1-\beta}^2\, u_{rel}^2(w) \right) A^{\#2} &- 2\, A^*\, A^{\#} + A^{*2} = k_{1-\beta}^2\, w^2 \left( \frac{A^{\#}}{w t_s} + \frac{r_0}{t_s} + \frac{r_0}{t_0} \right)
\end{aligned} \tag{B.10}$$

When $k_{1-\alpha} = k_{1-\beta} = k$, then we obtain the following from Equation (B.9):

$$A^{*2} = k\, w \left( \frac{r_0}{t_s} + \frac{r_0}{t_0} \right)$$

Next, substitute this expression into Equation (B.10):

$$\left( 1 - k^2\, u_{rel}^2(w) \right) A^{\#2} - 2A^* A^{\#} + Aa^{*2} = \frac{k^2\, w}{t_s} Aa^{\#} + A^{*2}$$

$$\left( 1 - k^2\, u_{rel}^2(w) \right) A^{\#2} - \left( 2A^* + \frac{k^2\, w}{t_s} \right) A^{\#} = 0$$

By solving the quadratic equation, the lower detection limit is obtained:

$$A^{\#} = \frac{2A^* + (k^2\, w)/t_s}{1 - k^2\, u_{rel}^2(w)} \tag{B.11}$$

$A^{\#}$ : Lower detection limit (Bq or Bq/kg, Bq/L, etc.)

$k$ : Coverage factor $k = k_{1-\alpha} = k_{1-\beta}$

$k_{1-\beta}$ : Coefficient for preventing Type-II errors (i.e., errors arising from failing to detect an effect or signal that actually exists)
Generally, $\alpha = \beta = 0.05$ (5%; $k_{1-\alpha} = k_{1-\beta} \fallingdotseq 1.645$).

$u_{rel}(w)$ : Relative standard uncertainty of the conversion factor $w$.

This is the relative standard uncertainty that combines all uncertainties associated with the measurement, excluding those pertaining to statistical counting.

## B.2 Lower Detection Limit in Kaiser's Method

When the sample being measured contains no radioactive nuclides at all, the net background count value distribution is as shown in Figure I.B.5. Let the net counting rate be $r_n$ and the statistical uncertainty of the count be $\sigma$. The detection limit is defined as the counting rate at which the detectable limit is $r_{DL} = k\sigma$.

$$r_{DL} = k\sigma \tag{B.12}$$

$\sigma$ : Uncertainty related to counting

$k$ : Coverage factor (often set to 3)

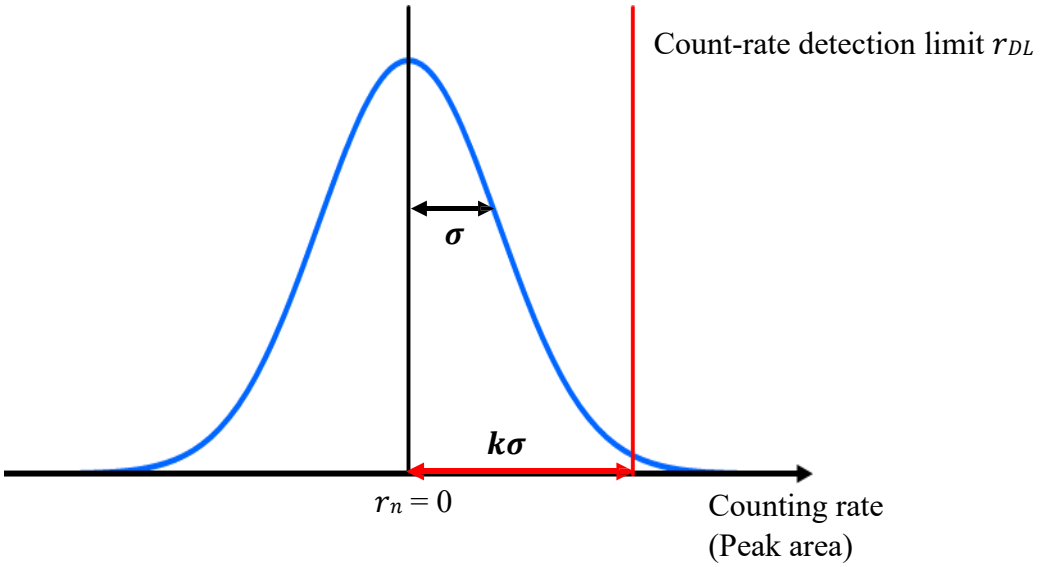



Figure I.B.5 Conceptual diagram of the detection limit determined using Kaiser's method

$r_{DL}$ and $\sigma$ are expressed by the following equations:

$$r_{DL} = r_s - r_0, \tag{B.13}$$

$$\sigma^2 = \frac{r_s}{t_s} + \frac{r_0}{t_0} \tag{B.14}$$

$r_s$ : Total counting rate of the sample (cps)

$r_0$ : Background counting rate (cps)

$t_s$ : Sample measurement time (s)

$t_0$ : Background measurement time (s)

Substituting Equations (B.13) and (B.14) into Equation (B.12) and solving the quadratic equation for $r_{DL}$ yields the count-rate detection limit:

$$r_{DL} = \frac{\frac{k^2}{t_s} + k\sqrt{(\frac{k}{t_s})^2 + 4r_0\left(\frac{1}{t_s} + \frac{1}{t_0}\right)}}{2} \tag{B.15}$$

The counting rate obtained at the detection limit is converted to radioactivity or radioactivity concentration and used as the lower detection limit.

## B.3 Calculation Example of the Lower Detection Limit

In this example, the detection limit is calculated using Kaiser's method and ISO 11929.

Measurement conditions (LBC measurement)

| | |
|---|---|
| Analysis sample | Water |
| Sample quantity $W_s$ | 49.689 (mL) |
| Sample measurement time $t_s$ | 18000 (s) |
| Sample count value $N_s$ | 9845 (count) |
| Background measurement time $t_0$ | 36000 (s) |
| Background count value $N_0$ | 81 (count) |
| Sample recovery rate $Y_I$ | 90.26 (%) |
| Sample detection efficiency $\varepsilon$ | 2.978 (%) |
| Relative uncertainty related to weighing $u_{rel}(weighing)$ | 0.0002 (%) |
| Relative uncertainty related to carrier addition $u_{rel}(carrier)$ | 0.06 (%) |
| Relative uncertainty related to the recovery rate $u_{rel}(Y)$ | 0.07 (%) |
| Relative uncertainty related to measuring instrument calibration $urel(\varepsilon)$ | 3.39 (%) |
| Half-life of $^{129}$I $T_{1/2}$ | $1.57 \times 10^7$ (years) |

(1) The sample counting rate $r_s$ (cps) and the background counting rate $r_0$ (cps) are as follows:

$$r_s = {}^{N_s}/_{t_s}$$
$$= {}^{9845}/_{18000} = 0.54694$$
$$r_0 = {}^{N_0}/_{t_0}$$
$$= {}^{81}/_{36000} = 0.00225$$

Therefore, the net counting rate $r_n$ (cps) and its uncertainty $u(r_n)$ are as follows:

$$r_n = r_s - r_0$$
$$= 0.54694 - 0.00225 = 0.54469,$$
$$u(r_n) = \sqrt{\frac{r_s}{t_s} + \frac{r_0}{t_0}}$$
$$= \sqrt{\frac{0.54694}{18000} + \frac{0.00225}{36000}} = 0.005518$$

(2) To obtain the half-life correction factor $DF$, it is necessary to determine the elapsed time $E$ (years) from sample collection to measurement. However, the elapsed time is much shorter than the half-life of $^{129}$I ($1.57 \times 10^7$ years). Therefore, the effect of decay can be neglected, allowing it to be approximated as zero.

$$DF = \exp\left(\frac{\ln(0.5) \times E}{T_{1/2}}\right)$$
$$\fallingdotseq \exp\left(\frac{\ln(0.5) \times 0}{1.57 \times 10^7}\right) = 1$$

(3) The conversion factor $w$ (/mL), its standard uncertainty $u(w)$, and the relative standard uncertainty $u_{rel}(w)$ are determined as follows:

$$w = \frac{1}{\varepsilon \times Y_I \times d \times m}$$
$$= \frac{1}{2.978/_{100} \times 90.26/_{100} \times 1 \times 49.689} = 0.7487$$
$$u(w) = w\sqrt{u_{rel}^2(weighting) + u_{rel}^2(carrier) + u_{rel}^2(Y) + u_{rel}^2(\varepsilon)}$$
$$= 0.7487 \times \sqrt{\left(\frac{0.0002}{100}\right)^2 + \left(\frac{0.06}{100}\right)^2 + \left(\frac{0.07}{100}\right)^2 + \left(\frac{3.39}{100}\right)^2} = 0.02539$$
$$u_{rel}(w) = \frac{u(w)}{w}$$
$$= \frac{0.02539}{0.7487} = 0.03391$$

(4) The radioactivity concentration $A$ (Bq/mL) and the combined standard uncertainty $u(A)$ (Bq/mL) are then obtained as follows:

$$A = r_n \times w$$
$$= 0.54469 \times 0.7487 = 0.4078$$
$$u(A) = A \times \sqrt{\left(\frac{u(r_n)}{r_n}\right)^2 + \left(\frac{u(w)}{w}\right)^2}$$
$$= 0.4078 \times \sqrt{\left(\frac{0.005518}{0.54469}\right)^2 + \left(\frac{0.02539}{0.7487}\right)^2} = 0.01443$$

First, the lower detection limit is determined using Kaiser's method. For this purpose, the count-rate detection limit

$$r_{DL} = \frac{\frac{k^2}{t_s} + k\sqrt{(\frac{k}{t_s})^2 + 4\,r_0\,(\frac{1}{t_s} + \frac{1}{t_0})}}{2}$$
$$= \frac{\frac{3^2}{18000} + 3\sqrt{(\frac{3}{18000})^2 + 4 \times 0.00225 \times (\frac{1}{18000} + \frac{1}{36000})}}{2}$$
$$= 0.001573$$

Furthermore, using the sample quantity and counting efficiency, it is converted into the radioactivity concentration. Then, the detection limit $A^{\#}_{Kaiser}$ (Bq/mL) is obtained:

$$A^{\#}_{Kaiser} = \frac{r_{DL}}{W_s \times \varepsilon \times Y_I}$$

$$= \frac{0.0015729}{49.689 \times {2.978}/{100} \times {90.26}/{100}} = 0.001178$$

Next, the lower detection limit $A^{\#}_{ISO11929}$ (Bq/mL) according to ISO 11929 is obtained together with the decision threshold $A^*$ (Bq/mL) from Equations (B.9) and (B.11) (here, $k$ = 1.645):

$$A^* = k_{1-\alpha} \times w \times \sqrt{\frac{N_0}{t_0\, t_s} + \frac{N_0}{{t_0}^2}}$$

$$= 1.645 \times 0.7487 \times \sqrt{\frac{81}{36000 \times 18000} + \frac{81}{36000^2}} = 0.0005333$$

$$A^{\#}_{ISO11929} = \frac{2\,A^* + \frac{k^2 \times w}{t_s}}{1 - k^2 \times u^2_{rel}(w)}$$

$$= \frac{2 \times 0.0005333 + \frac{1.645^2 \times 0.7487}{18000}}{1 - 1.645^2 \times 0.03391^2} = 0.001183$$

These results are summarized in Table I.B.1.

Table I.B.1 Lower detection limit for each parameter and each calculation method

| Parameter | | Kaiser's method | ISO 11929 |
|---|---|---|---|
| Radioactivity concentration | $A$ (Bq/mL) | 0.4078 | |
| Combined standard uncertainty | $u(A)$ (Bq/mL) | 0.014 | |
| Decision threshold | $A^*$ (Bq/mL) | 0.001178※1 | 0.0005333 |
| Lower detection limit | $A^{\#}$ (Bq/mL) | 0.001178 | 0.001183 |

※1 In Kaiser's method, the decision threshold is equal to the detection limit.

## Explanation C : Estimation of $^{129}$I Concentrations in Polished Rice, Leafy Vegetables, and Potatoes Based on $^{129}$I Concentrations in Soil

The concentration of $^{129}$I in biological samples is often low and undetectable. Nevertheless, it can be estimated from the $^{129}$I concentration in the soil used during cultivation using the following equation:

$$A_{crop} = A_{soil} \times TF.$$

$A_{crop}$ : Concentration of $^{129}$I in the biological sample (Bq/g)

$A_{soil}$ : Concentration of $^{129}$I in the soil sample (Bq/g)

$TF$ : Transition coefficient

The normal transition coefficient is 0.002[*160] for polished rice and 0.003–0.016[*161] for leafy vegetables.

The transfer coefficient of $^{129}$I between potatoes and soil samples collected in the Fukushima Prefecture in 2019 following the "1F accident" was reported to be 0.00021 (geometric mean)[*162].

[*160] Y.Muramatsu et al.: Some considerations on the sorption and desorption phenomena of iodine and iodate on soil, Water, Air and Soil Pollution, 521, 157-171 (1989)

[*161] Y.Muramatsu et al.: Tracer experiments on the behavior of radioiodine in the soil-plant-atmosphere system, Journal of radioanalytical and nuclear chemistry, 194, 303-310 (1995)

[*162] 塚田祥文: 分担研究報告書1 農作物中Cs と長半減期核種の濃度測定に関する研究 (研究課題名: 食品中の放射性物質濃度の基準値に対する放射性核種濃度比の検証とその影響評価に関する研究), 2020 年度 厚生労働科学研究費補助金 健康安全確保総合研究分野 食品の安全確保推進研究 (2021)

# Appendix

## Analysis Flow

(1) Airborne particulate matter

(1)-1. Combustion–activated carbon adsorption method

① Pretreatment

Use a filter paper and an activated-carbon filter paper or cartridge

|

Place it inside the inner tube of a quartz tube (place quartz wool at both ends).

|

← Add the iodine carrier solution (20 mgI/mL; 1 mL)

② Combustion of samples

Place 3 g of activated carbon in the outer tube (with quartz wool placed at both ends). Pack quartz wool containing copper oxide into the section where Electric Furnace (B) is located.

|

Attach the outer tube to the combustion device and the inner tube to the outer tube.

|← Operate Electric Furnace (C) at 150 °C

Combustion

|← Inner tube (supply nitrogen gas at 100 mL/min)

|← Outer tube (supply oxygen gas at 200 mL/min)

|← Operate Electric Furnace (B) at 1000 °C

Move Electric Furnace (A) to the right end of the sample

|

← Operate Electric Furnace (A) at 240 °C

Move Electric Furnace (A) toward Electric Furnace (B)

|

Electric Furnace (A) comes into contact with Electric Furnace (B)

|← Operate Electric Furnace (A) at 280 °C for 1 hour

|← Operate Electric Furnace (A) at 350°C for 2–3 hours

Move Electric Furnace (A) to the right end of the sample

|← Operate Electric Furnace (A) at 400 °C

|← Inner tube (supply oxygen gas at 50 mL/min)

Move Electric Furnace (A) toward Electric Furnace (B) (reduce nitrogen-gas flow rate in the inner tube)

|← Operate Electric Furnace (A) at 600 °C

|← Inner tube (supply oxygen gas at 100 mL/min)

When Electric Furnace (A) touches Electric Furnace (B), move Electric Furnace (A) to the center of the sample.

← Operate Electric Furnace (A) at 1000 ℃

← Operate Electric Furnace (B) at 500 ℃

← Turn Electric Furnace (A) off

Sample combustion complete

Combustion of iodine-adsorbed activated carbon

Place 0.5 g of new activated carbon into a trap tube (with quartz wool filled at both ends).

Connect the trap tube to the left end of the outer tube.

Then, connect the trap tube to Electric Furnace (C) and the right end of (D) to the left end of Electric Furnace (B).

← Outer tube/inner tube (supply oxygen gas at 50 mL/min)

Move Electric Furnace (B) to the left

Completion of activated carbon (3 g) combustion

③ Chemical separation of iodine after combustion

Place 0.5 g of activated carbon into a 50 mL Erlenmeyer flask

← Add the sodium hydroxide solution (24 w/v%; 20 mL)

Attach the air cooling pipe, followed by heating and leaching

Cool the mixture

Suction filtration

Transfer 100 mL of the filtrate into a separatory funnel — Discard the residue

← Add xylene (20 mL)

← Nitric acid (8 mL; adjusted to pH 1)

← Sodium nitrite solution (10 w/v%; 5 mL)

Shake vigorously (2 minutes)

Transfer the organic phase to a different 100 mL separatory funnel — Aqueous phase

← Add xylene (20 mL)

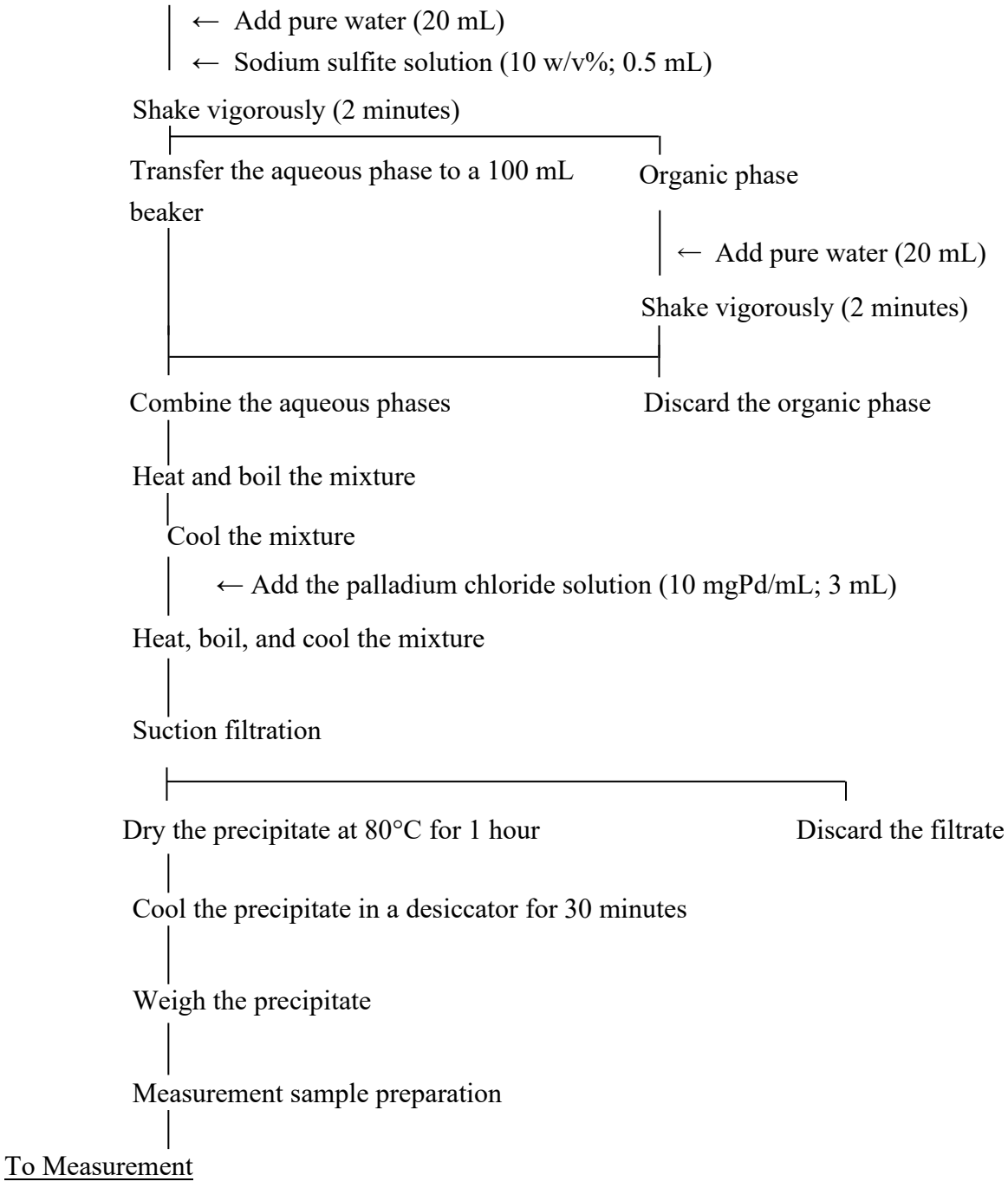
Shake vigorously (2 minutes)

Combine the organic phases — Discard the aqueous phase

← Add pure water (20 mL)

Shake vigorously (2 minutes)

Organic phase — Discard the aqueous phase


← Add pure water (20 mL)
← Sodium sulfite solution (10 w/v%; 0.5 mL)
Shake vigorously (2 minutes)
Transfer the aqueous phase to a 100 mL beaker
Organic phase
← Add pure water (20 mL)
Shake vigorously (2 minutes)
Combine the aqueous phases
Discard the organic phase
Heat and boil the mixture
Cool the mixture
← Add the palladium chloride solution (10 mgPd/mL; 3 mL)
Heat, boil, and cool the mixture
Suction filtration
Dry the precipitate at 80°C for 1 hour
Discard the filtrate
Cool the precipitate in a desiccator for 30 minutes
Weigh the precipitate
Measurement sample preparation
To Measurement

(1)-2. Combustion–alkali solution absorption method

① Pretreatment

Same as "① Pretreatment" in "(1)-1. Combustion–activated carbon adsorption method"

② Combustion of samples

Prepare two 200 mL gas washing bottles and attach them to the outer tube

1 Step 1: Add pure water (180 mL), potassium hydroxide (10 g), and potassium sulfite (1 g)

2 Step 2: Add pure water (90 mL), potassium hydroxide (5 g), and potassium sulfite (0.5 g)

Attach the inner tube to the outer tube, which is packed with quartz wool containing copper oxide in the section where Electric Furnace (B) is located.

Then, connect the outer tube to the combustion device.

← Inner tube (supply nitrogen gas at 100 mL/min)

← Outer tube (supply oxygen gas at 200 ml/min)

← Operate Electric Furnace (B) at 1000°C

Combustion

Move Electric Furnace (A) to the right edge of the sample

← Operate Electric Furnace (A) at 240°C

Move Electric Furnace (A) toward Electric Furnace (B)

Electric Furnace (A) comes into contact with Electric Furnace (B)

← Operate Electric Furnace (A) at 280 °C for 1 hour

← Operate Electric Furnace (A) at 350 °C for 2–3 hours

Move Electric Furnace (A) to the right edge of the sample

← Operate Electric Furnace (A) at 400 °C

← Inner tube (supply oxygen gas at 50 mL/min)

Move Electric Furnace (A) toward Electric Furnace (B) (reduce nitrogen-gas flow rate in the inner tube)

← Operate Electric Furnace (A) at 600 °C

← Inner tube (supply oxygen gas at 100 mL/min)

When Electric Furnace (A) touches Electric Furnace (B), move Electric Furnace (A) to the center of the sample

← Operate Electric Furnace (A) at 1000 °C

← Turn Electric Furnaces (A) and (B) off

Sample combustion complete

↓

Remove the washing bottle

↓

Transfer the solution from the washing bottle to a 500 mL beaker

③ Chemical separation of iodine after combustion

Heat and concentrate the solution (up to 50 mL)

↓

Transfer 100 mL of the filtrate into a separatory funnel

← Add xylene (20 mL)

← Add nitric acid (18 mL; adjusted to pH 1)

← Add the potassium sulfite solution (10 w/v%; 5 mL)

Shake vigorously (2 minutes)

Transfer the organic phase to a 100 mL separatory funnel

Aqueous phase

← Add xylene (20 mL)

Shake vigorously (2 minutes)

Combine the organic phases

Discard the aqueous phase

← Add pure water (20 mL)

Shake vigorously (2 minutes)

Organic phase

Discard the aqueous phase

← Add pure water (20 mL)

← Add the potassium sulfite solution (10 w/v%; 0.5 mL)

Shake vigorously (2 minutes)

Transfer the aqueous phase to a 100 mL beaker

Organic phase

← Add pure water (20 mL)

Shake vigorously (2 minutes)

Combine the aqueous phases

Discard the organic phase

↓

Heat and boil the mixture

↓

Cool the mixture

← Add the palladium chloride solution (10 mgPd/mL; 3 mL)

Heat and boil the mixture

↓

Cool the mixture

↓

Suction filtration

Dry the precipitate at 80°C for 1 hour — Discard the filtrate

Measure the weight of the precipitate after cooling for 30 minutes in a desiccator

Measurement sample preparation

To Measurement

(2) Inland water and milk samples

(2)-1. Combustion–activated carbon adsorption method

① Adsorption onto an anion-exchange resin

Take 5 L of an inland water or milk sample

Transfer it to a 5 L beaker

← Add the iodine carrier solution (20 mgI/mL; 1 mL)

← Add the sodium sulfite solution (10 w/v%; 0.5 mL)

← Add the anion-exchange resin (50 mL)

Stir for 30 minutes and settle for 30 minutes

Decantation

Transfer the resin to a 500 mL beaker — Transfer the sample to another 5 L beaker

← Add 50 mL of the anion-exchange resin

Stirring (30 minutes) and settling (30 minutes)

Decantation

Combine the resins — Discard the samples

← Add warm pure water (60 °C–70 °C; 300 mL)

Decantation

Stir for a few seconds and let the solution settle

Repeat until the washing solution becomes clear

Resin — Discard the supernatant

② Combustion of samples

Dry the resin at 70 °C (to the point when it is slightly moist)

Spread a small amount inside the inner tube of the quartz tube
(prepack the narrower end of the inner tube with quartz wool)

Same as "② Combustion of samples" in "(1)-1. Combustion–activated carbon adsorption method"

③ Chemical separation of iodine after combustion

Same as "③ Chemical separation of iodine after combustion" in "(1)-1. Combustion–activated carbon adsorption method"

(2)-2. Combustion–alkali solution absorption method

① Adsorption onto an anion-exchange resin

Same as "① Adsorption onto an anion-exchange resin" in "(2)-1. Combustion–activated carbon adsorption method"

② Combustion of samples

Dry the resin (at 70 °C)

|

Spread a small amount inside the inner tube (with quartz wool placed at both ends)

|

Same as "② Combustion of samples" in "(1)-2. Combustion–alkali solution absorption method"

③ Chemical separation of iodine after combustion

Same as "③ Chemical separation of iodine after combustion" in "(1)-2. Combustion–alkali solution absorption method"

(2)-3. Sodium hypochlorite elution method

(1) Adsorption onto an anion-exchange resin

Same as "① Adsorption onto an anion-exchange resin" in "(2)-1. Combustion–activated carbon adsorption method"

② Elution from the anion-exchange resin

Take the cleaned resin

← Add the sodium hypochlorite solution (100 mL)

Mixing for 5 minutes

Suction filtration

Transfer the filtrate to a 500 mL beaker

Transfer the resin to another 300 mL beaker

← Add the sodium hypochlorite solution (100 mL)

Mixing for 5 minutes

Suction filtration

Combine the filtrates

Discard the resin

← Add sulfuric acid (9 mol/L; 48 mL)

Stir until no bubbles remain

← Add sulfuric acid (9 mol/L; 48 mL)

Heating

Cooling

③ Chemical separation of iodine after elution

Take the sodium hypochlorite solution obtained after elution

← Add pure water (up to 400 mL)

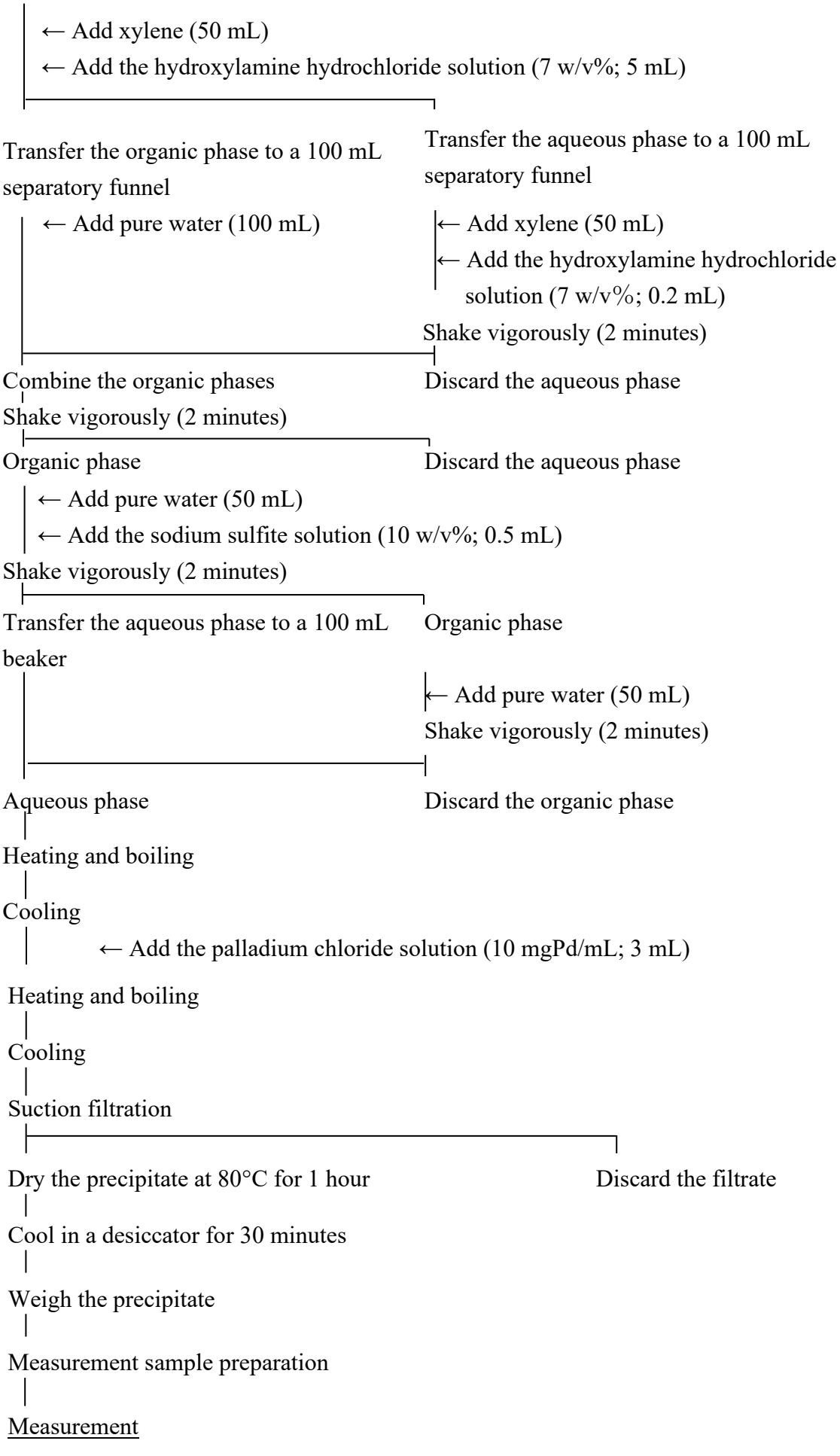
Transfer to a 500 mL separating funnel

← Add xylene (20 mL)

Shake vigorously (1 minute)

Transfer the aqueous phase to a 500 mL separatory funnel

Discard the organic phase


← Add xylene (50 mL)
← Add the hydroxylamine hydrochloride solution (7 w/v%; 5 mL)
Transfer the organic phase to a 100 mL separatory funnel
Transfer the aqueous phase to a 100 mL separatory funnel
← Add pure water (100 mL)
← Add xylene (50 mL)
← Add the hydroxylamine hydrochloride solution (7 w/v%; 0.2 mL)
Shake vigorously (2 minutes)
Combine the organic phases
Discard the aqueous phase
Shake vigorously (2 minutes)
Organic phase
Discard the aqueous phase
← Add pure water (50 mL)
← Add the sodium sulfite solution (10 w/v%; 0.5 mL)
Shake vigorously (2 minutes)
Transfer the aqueous phase to a 100 mL beaker
Organic phase
← Add pure water (50 mL)
Shake vigorously (2 minutes)
Aqueous phase
Discard the organic phase
Heating and boiling
Cooling
← Add the palladium chloride solution (10 mgPd/mL; 3 mL)
Heating and boiling
Cooling
Suction filtration
Dry the precipitate at 80°C for 1 hour
Discard the filtrate
Cool in a desiccator for 30 minutes
Weigh the precipitate
Measurement sample preparation
Measurement

(3) Seawater

Take a seawater sample (5 L)

← Add the iodine carrier solution (20 mgI/mL; 1 mL)

← Add sulfuric acid (3 mol/L; 20 mL)

← Add the hydrazinium sulfate saturated solution (40 mL)

Stir and let the mixture settle for 10 minutes

← Add the silver nitrate solution (0.3 w/v%; 100 mL; add gradually while stirring)

Silver iodide precipitate

Suction filtration

Transfer the precipitate along with the filter paper to a 300 mL beaker — Discard the filtrate

← Add pure water (50 mL)

← Add powdered zinc (1 g)

← Add sulfuric acid (3 mol/L; 0.5 mL)

Heat for 1 minute

Suction filtration

Transfer the filtrate to a 300 mL separatory funnel — Discard the residue

← Add xylene (20 mL)

← Add nitric acid (2 mol/L; 1 mL)

← Add the sodium nitrite solution (10 w/v%; 1 mL)

Shake vigorously (2 minutes)

Transfer the organic phase to a 100 mL separatory funnel

Transfer the aqueous phase to a 100 mL separatory funnel

← Add xylene (20 mL)

Shake vigorously (2 minutes)

Combine the organic phases

Discard the aqueous phase

← Add pure water (20 mL)

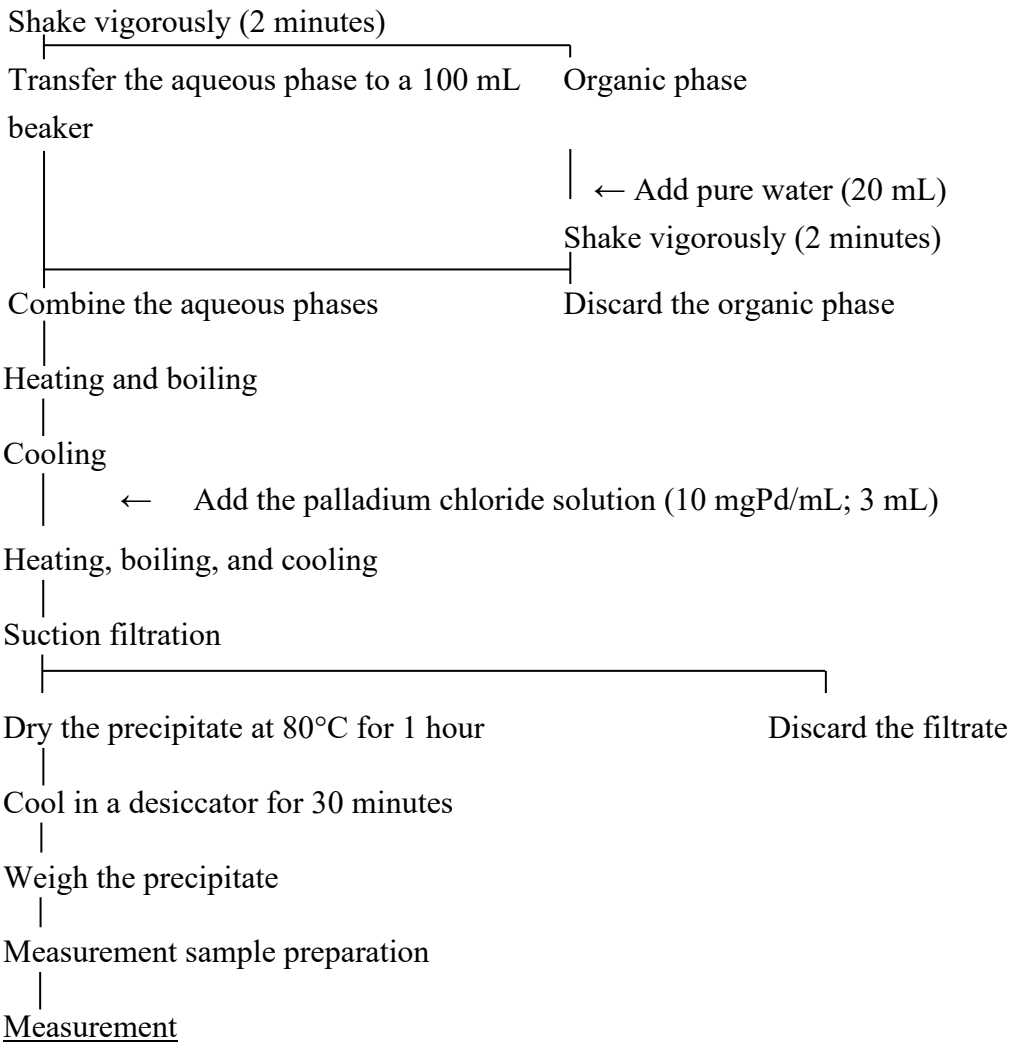
Shake vigorously (2 minutes)

Organic phase

Discard the aqueous phase

← Add pure water (20 mL)

← Add the sodium sulfite solution (10 w/v%; 0.2 mL)


Shake vigorously (2 minutes)
Transfer the aqueous phase to a 100 mL beaker
Organic phase
← Add pure water (20 mL)
Shake vigorously (2 minutes)
Combine the aqueous phases
Discard the organic phase
Heating and boiling
Cooling
← Add the palladium chloride solution (10 mgPd/mL; 3 mL)
Heating, boiling, and cooling
Suction filtration
Dry the precipitate at 80°C for 1 hour
Discard the filtrate
Cool in a desiccator for 30 minutes
Weigh the precipitate
Measurement sample preparation
Measurement

(4) Soil

(4)-1. Combustion–activated carbon adsorption method

① Pretreatment

Take a soil sample

|

Dry (70 °C) and pulverize

|

Weigh

|

Place inside the inner tube (with quartz wool placed at both ends)

| ← Add the iodine carrier solution (20 mgI/mL; 1 mL)

(Next step)

② Combustion of samples

Place 3 g of activated carbon in the outer tube (with quartz wool placed at both ends)

Pack quartz wool containing copper oxide into the section where Electric Furnace (B) is located

|

Attach the outer tube to the combustion device and the inner tube to the outer tube

| ← Operate Electric Furnace (C) at 150 °C

| ← Operate Electric Furnace (B) at 1000 °C

| ← Inner tube (supply oxygen gas and nitrogen gas both at 50 mL/min)

| ← Outer tube (supply oxygen gas at 200 mL/min)

Place Electric Furnace (A) at the right end of the sample

| ← Operate Electric Furnace (A) at 250 °C

Combustion

|

Move Electric Furnace (A) toward Electric Furnace (B)

|

When Electric Furnace (A) touches Electric Furnace (B), move Electric Furnace (A) to the right end of the sample

| ← Operate Electric Furnace (A) at 700°C

Move Electric Furnace (A) toward Electric Furnace (B)

|

When Electric Furnace (A) touches Electric Furnace (B), move Electric Furnace (A) to the center of the sample

| ← Operate Electric Furnace (A) at 1000 °C for 2 hours

| ← Operate Electric Furnace (B) at 500 °C

| ← Turn Electric Furnace (A) off

Sample combustion complete

Combustion of iodine-adsorbed activated carbon

|

Place 0.5 g of new activated carbon into a trap tube (with quartz wool placed at both

ends).

↓

Connect the trap tube to the left end of the outer tube.

Set the trap tube to Electric Furnace (C), and connect the right end of (D) to the left end of Electric Furnace (B)

↓

Move Electric Furnace (B) to the left

↓

Completion of activated carbon (3 g) combustion

③ Chemical separation of iodine after combustion

Same as "③ Chemical separation of iodine after combustion" in "(1)-1. Combustion–activated carbon adsorption method"

(4)-2. Combustion–alkali solution absorption method

① Pretreatment

Same as "① Pretreatment" in "(4)-1. Combustion–activated carbon adsorption method"

② Combustion of samples

Prepare two 200 mL gas washing bottles and attach them to the outer tube

1 Step 1: Add pure water (180 mL), potassium hydroxide (10 g), and potassium sulfite (1 g)

2 Step 2: Add pure water (90 mL), potassium hydroxide (5 g), and potassium sulfite (0.5 g)

Pack quartz wool containing copper oxide into the section where Electric Furnace (B) is located

|

Attach the outer tube to the combustion device and the inner tube to the outer tube

| ← Inner tube (supply nitrogen gas at 100 mL/min)

| ← Outer tube (supply oxygen gas at 200 mL/min)

| ← Operate Electric Furnace (B) at 1000 °C

Move Electric Furnace (A) to the right edge of the sample

| ← Operate Electric Furnace (A) at 1000 °C

Move Electric Furnace (A) toward Electric Furnace (B) (for 2 hours)

| ← Turn Electric Furnaces (A) and (B) off

Sample combustion complete

|

Remove the washing bottle

|

Transfer the solution from the washing bottle to a 500 mL beaker.

③ Chemical separation of iodine after combustion

Same as "③ Chemical separation of iodine after combustion" in "(1)-2. Combustion–alkali solution absorption method"

(5) Vegetables, polished rice, and seaweed

(5)-1. Combustion–activated carbon adsorption method

① Pretreatment of samples

1) Vegetable

Take a vegetable sample (1 kg)
|
Dry (70 °C) and pulverize
|
Weigh
|
Place inside the inner tube (with quartz wool placed at both ends)
| ← Add the iodine carrier solution (20 mgI/mL; 1 mL) (go to Step)

2) Polished rice

Take a sample of polished rice (1 kg)
|
Pulverize and weigh
|
Place inside the inner tube (with quartz wool placed at both ends)
| ← Add the iodine carrier solution (20 mgI/mL; 1 mL) (go to Step)

3) Seaweed

Take a seaweed sample (1 kg)
|
Dry (70 °C) and pulverize
|
Weigh
Place inside the inner tube (with quartz wool placed at both ends)
| ← Add the iodine carrier solution (20 mgI/mL; 1 mL) (go to Step ②)

② Combustion of samples

Same as "② Combustion of samples" in "(1)-1. Combustion–activated carbon adsorption method"

③ Chemical separation of iodine after combustion

Same as "③ Chemical separation of iodine after combustion" in "(1)-1. Combustion–activated carbon adsorption method"

(5)-2. Combustion–alkali solution absorption method

① Pretreatment of samples

Same as "① Pretreatment" in "(5)-1. Combustion–Activated Carbon Adsorption

Method”

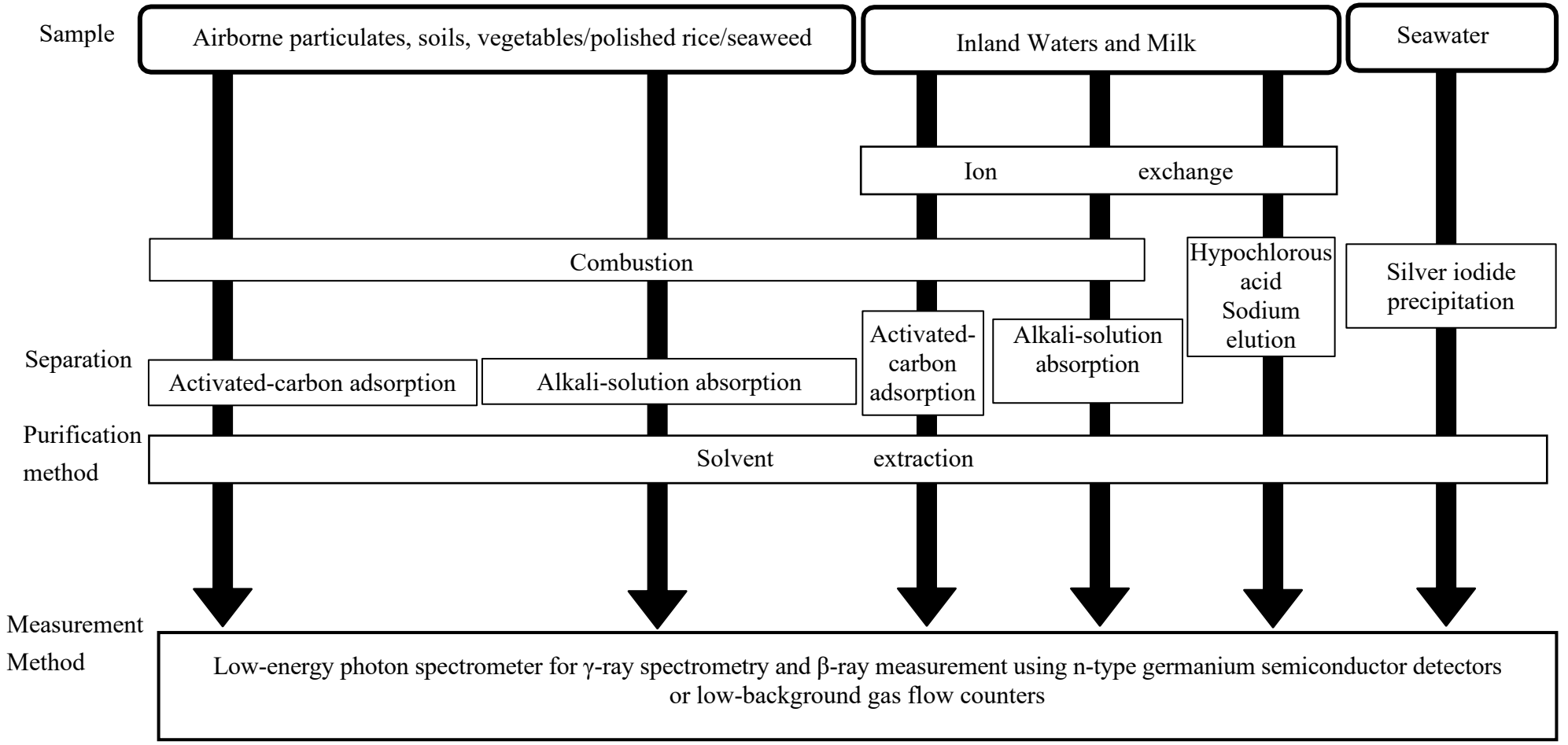
② Combustion of samples

Same as “② Combustion of samples” in “(1)-2. Combustion–alkali solution absorption method”

③ Chemical separation of iodine after combustion

Same as “③ Chemical separation of iodine after combustion” in “(1)-2. Combustion–alkali solution absorption method”

Radiochemical Analysis




Appendix I.1 Measurement of $^{129}I$ using radiochemical analysis

# II. Triple Quadrupole ICP–MS

# Chapter 1 Seawater

Collected seawater samples should be filtered and analyzed without the addition of acids or other chemical reagents. After appropriate dilution, the $^{129}I$ concentration should be quantified using triple quadrupole ICP–MS. To confirm the reliability of the analytical procedure, it is recommended to additionally measure the $^{127}I$ concentration[*163,*164,*165].

In seawater monitoring conducted under the Comprehensive Radiation Monitoring Plan, the target detection limit is set at 0.01–1.2 Bq/L. Therefore, the dilution ratio must be selected to achieve this level of sensitivity. Additionally, as seawater salinity is typically ~3%, dilution should reduce the salt content to <0.1% to enable stable measurement under standard plasma conditions.

Table II.1.1 presents example dilution factors and their corresponding detectable levels. In this method, a 50-fold dilution was used, which sufficiently met the required detection limit and lowered the effective salt concentration to <0.1%.

The nebulizer, an element of the sample introduction system used for ICP–MS, has a fine tube that converts the sample into an aerosol. To avoid blockage caused by insoluble residues or particulate matter, sample filtration is advised. Common filtration approaches include vacuum filtration and syringe filtration. Because syringe filtration requires only a small sample volume and shows operational simplicity and high efficiency, it was adopted for filtration.

Table II.1.1 Detectable levels of $^{129}I$ in seawater samples

| Dilution factor | Salt concentration (%)※1 | Detectable level (Bq/L)※2 | Detectable $^{129}I/^{127}I$ isotopic ratio ※3,※4 | Target lower detection limit [Isotopic ratio※3,※4] (Bq/L)※5 |
|---|---|---|---|---|
| 1000 | 0.003 | 0.1 | $3 \times 10^{-4}$ | 0.01–1.2 [$3 \times 10^{-5}$ to $3 \times 10^{-3}$] |
| 100 | 0.03 | 0.01 | $3 \times 10^{-5}$ | |
| 50 | 0.06 | 0.007 | $2 \times 10^{-5}$ | |
| 10 | 0.3 | 0.001 | $3 \times 10^{-6}$ | |

※1 A seawater salinity of 3% was used as the basis for calculation.

※2 The method detection limit was set to 0.02 ng/L using a specific activity of $6.53 \times 10^6$ Bq/g.

※3 The $^{129}I/^{127}I$ isotopic ratio was determined as the ratio of either the detectable $^{129}I$ level or the target detection limit to the $^{127}I$ concentration in seawater.

※4 The $^{127}I$ concentration in seawater was assumed to be 0.06 mg/L.

※5 Target detection limits correspond to values specified in monitoring surveys conducted under the Comprehensive Radiation Monitoring Plan.

*163 The concentration of $^{127}I$ in seawater is approximately 0.06 mg/L.

*164 For seawater collected from the same sampling location, it is recommended to monitor potential long-term fluctuations in the $^{127}I$ concentration.

*165 For detailed methodology on $^{127}I$ determination, refer to "Explanation B Determination of $^{127}I$."

## 1.1 Equipment, Instruments, and Reagents

Reagent masses and volumes specified here are indicative of preparation ratios. Adjust quantities as needed at the time of preparation. Use reagents compliant with the JIS. When no standard is specified, select the highest available reagent grade.

(1) Equipment

1) Ultrapure water production system

(2) Instruments

1) Disposable syringe (without needle; 10 mL capacity; Figure II.1.1)
2) Syringe filter (hydrophilic; 0.45 $\mu$m pore size; Figure II.1.1)
3) Beaker or a polyethylene collection vessel for the filtrate
4) Micropipette (1 mL)
5) Pipette tips (1 mL)
6) Volumetric flask (50 mL)

(3) Reagents

1) Ultrapure water (purified to a resistivity of ≥18 MΩ·cm)[*166]
2) Tetramethylammonium hydroxide (TMAH) solution[*167,*168,*169] (mass fraction: 25%)

## 1.2 Analytical Operations

(1) Filtration of seawater

1) Fill a disposable syringe with seawater and attach the syringe filter.
2) Depress the syringe plunger to discharge the seawater sample, and rinse the syringe and filter.
3) Draw seawater into the syringe again and attach the filter.
4) Depress the plunger to discharge the seawater sample, collecting the filtered seawater in a container.

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[*166] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition No. 5218.

[*167] 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 about handling these substances.

[*168] 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." Further, necessary measures must be implemented to prevent theft, loss, leakage, or other incidents.

[*169] Classified as a Category IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Use of open flames is strictly prohibited. Store and handle below the flash point. Keep away from Category I and Category V Hazardous Materials. Further, take precautions against static electricity generation and avoid filling containers completely when repackaging (to prevent rupture due to thermal expansion).

(2) Preparation of measurement samples

1) Using a micropipette, collect 1 mL of the filtered seawater.
2) Add it to the 50 mL volumetric flask.
3) Add 1 mL of the TMAH solution (25%).
4) Add ultrapure water up to the calibration mark of the volumetric flask.
5) Shake thoroughly and use for $^{129}$I measurement[*170].

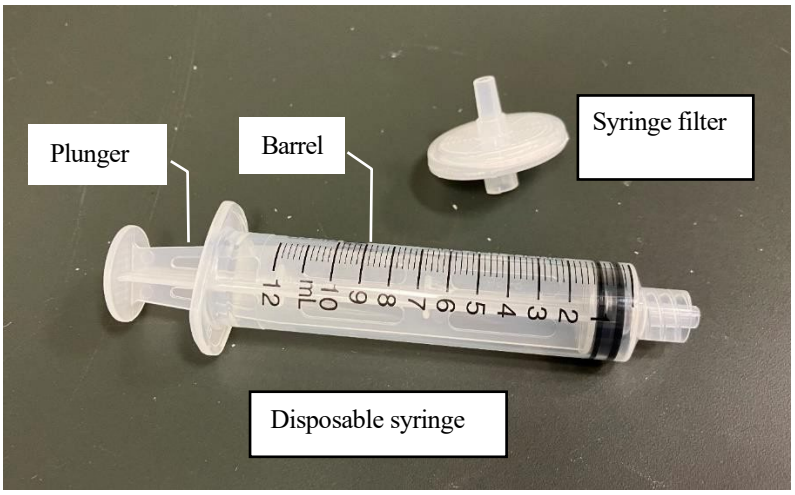



Figure II.1.1 Disposable syringe and a syringe Filter

[*170] When adding an internal standard, ensure that the final internal-standard concentration is 10 μg/L.

# Chapter 2 Seaweed

Freeze-dried seaweed[*171] samples should first be subjected to thermal hydrolysis. The iodine released during this process should be captured in an alkali absorption solution, which should be subsequently diluted to prepare the measurement sample. Triple quadrupole ICP–MS should be used to measure $^{129}I$ and determine the $^{129}I$ concentration in the sample. As with seawater analysis, the determination of $^{127}I$ is also recommended to verify the analytical process[*172,*173].

A key characteristic of seaweed samples is their typically elevated $^{127}I$ concentrations. This can lead to spectral interference at m/z 129 due to the formation of $I^1H_2$ ($^{127}I^2D$.) The ratio of $^{127}I^1H_2$ ($^{127}I^2D$) to $^{127}I$ (herein referred to as the $IH_2$ (ID) formation ratio[*174]) remains constant depending on instrumental conditions and measurement parameters. Therefore, by calculating the amount of $^{127}I^1H_2$ ($^{127}I^2D$) and correcting the measured values, the effect of the interference can be reduced (this process is referred to as $IH_2$ (ID) correction)[*175,*176]. This correction is valid only when the sample's $^{129}I/^{127}I$ isotopic ratio is equal to or greater than the correction threshold[*177], which is calculated as the $IH_2$ (ID) formation ratio + standard deviation. If the isotopic ratio falls below this threshold, the uncertainty becomes excessive and the correction is not reliable[*178].

The combination of the sample mass and dilution factor for $^{129}I$ analysis must satisfy all the following requirements:

(1) The detectable level for the combination should be below the target detection limit.

(2) The detectable $^{129}I/^{127}I$ isotopic ratio (calculated from the detectable limit and the $^{127}I$ concentration in the sample) should be equal to or exceed the correction threshold.

(3) The dilution factor should be sufficient enough to eliminate the effect of salts and maintain effective internal-standard correction.

*171 For freeze-drying, refer to The Series of Environmental Radioactivity Measuring Methods No. 9: "Tritium Analysis Method."

*172 For determination of $^{127}I$, refer to "Explanation B Determination of $^{127}I$."

*173 Representative examples of iodine concentrations and dry residues in various seaweeds are provided below.

| Seaweed | Iodine concentration (mg/kg raw) | Dry residue (%) |
|---|---|---|
| Amanori | 1 ～ 30 | 5 |
| Kombu | 30 ～ 1,300 | 20 |
| Hijiki | 30 ～ 530 | 20 |
| Wakame | 10 ～ 130 | 5 |

*174 For detailed calculation methods, refer to "3.4 Confirmation of the Dihydride Formation Ratio" in "Chapter 3 Measurement".

*175 For details of the correction method, refer to "3.5.1 Calculation of $^{129}I$ Radioactivity Concentration" in "Chapter 3 Measurement."

*176 For other countermeasures, refer to "A.1.1 (1) Measures against $^{127}I$ hydrides" in "Explanation A Interference Factors in Triple Quadrupole ICP–MS."

*177 For the calculation method, refer to "3.5.2 Determination of Correction Applicability" in "Chapter 3 Measurement."

*178 In calculations, a dihydride formation ratio of $8 \times 10^{-9}$ was considered. Meanwhile, Ohno et al. reported a value of $5 \times 10^{-9}$. (T. Ohno et al.: Determination of ultratrace $^{129}I$ in soil samples by Triple Quadrupole ICP-MS and its application to Fukushima soil samples, Journal of Analytical Atomic Spectrometry, 28, 1283-1287 (2013))
Since the measurement of isotopic ratios below $10^{-9}$ is considered difficult, if the target isotopic ratio is below $10^{-9}$, it is recommended to use AMS (see "III. AMS").

Increasing the sample mass or decreasing the dilution factor can increase the detectable level; however, these adjustments also lower the detectable isotopic ratio, which potentially falls below the correction threshold. Regarding dilution, high sodium sulfite concentrations may introduce interference at m/z 129[*179]. Further, in high-matrix samples, the uncertainty pertaining to internal-standard correction may increase[*180]. Therefore, a dilution factor of 50-fold or greater is necessary.

Table II.2.1 presents the detectable levels and detectable isotopic ratios for different combinations of sample amount and dilution factor for kombu, which is known for its high $^{127}I$ concentration, as an example. Figure II.2.1 shows the associated conceptual diagram. To satisfy the target detection limit of 0.1 Bq/kg (raw) specified in the Comprehensive Radiation Monitoring Plan and ensure that the detectable isotopic ratio remains equal to or exceeds the correction threshold, an analytical sample size of 0.6 g (dry) and 100-fold dilution were selected.

Table II.2.1 Examples of detectable levels of $^{129}I$ in seaweed samples

| Sample amount used for analysis (g; dry weight) | Dilution factor | Detectable level (Bq/kg; raw)※1,※2 | Detectable $^{129}I/^{127}I$ isotopic ratio※3, ※4, ※5 | Target lower detection limit [Isotopic ratio※3,※4] (Bq/kg raw) ※6 |
|---|---|---|---|---|
| 0.1 | 500 | 3 | $3 \times 10^{-7}$ | 0.1 [$1 \times 10^{-8}$] |
| | 100 | 0.5 | $6 \times 10^{-8}$ | |
| | 10 | 0.05 | $(6 \times 10^{-9})$ | |
| 0.6 | 2500 | 2 | $3 \times 10^{-7}$ | |
| | 100 | 0.09 | $1 \times 10^{-8}$ | |
| | 10 | 0.01 | $(1 \times 10^{-9})$ | |
| 2 | 5000 | 1 | $2 \times 10^{-7}$ | |
| | 100 | 0.03 | $(3 \times 10^{-9})$ | |
| | 10 | 0.003 | $(3 \times 10^{-10})$ | |

※1 The lower method detection limit was set to 0.02 ng/L and the specific activity set to $6.53 \times 10^6$ Bq/g.

※2 The weight ratio of dry matter to raw samples was set to 20%.

※3 The $^{129}I/^{127}I$ isotopic ratio was obtained by dividing the detectable level or target detection limit of $^{129}I$ by the $^{127}I$ concentration in the seaweed sample.

※4 The $^{127}I$ concentration in the seaweed sample was assumed to be 1300 mg/kg raw seaweed (for kombu).

※5 Isotopic ratios that did not meet the correction threshold ($9 \times 10^{-9}$) are shown in parentheses.

*179 Refer to "A.3 Examination of the Effects of Salts" in "Explanation A Interference Factors in Triple Quadrupole ICP–MS."

*180 Regarding changes in internal-standard correction resulting from dilution factors, refer to "E.2 $^{129}I$ Addition Test for the Selection of Internal Standard Elements" in "Explanation E Selection of Internal Standard-Elements."

※6 Target detection limit set in various surveys conducted under the Comprehensive Radiation Monitoring Plan.

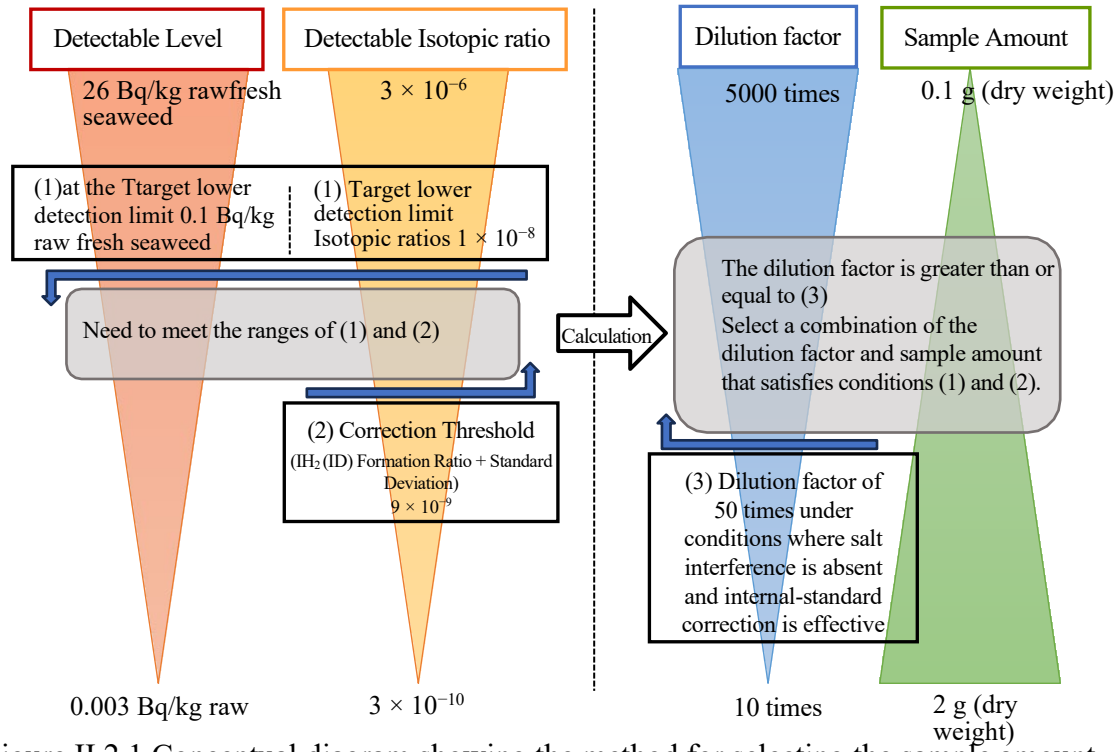



Figure II.2.1 Conceptual diagram showing the method for selecting the sample amount and dilution factor

## 2.1 Equipment, Instruments, and Reagents

Figure II.2.2 shows a schematic of the thermal hydrolysis method.

(1) Equipment

1) Tube-type electric furnace (with a temperature controller and gas flowmeter; maximum temperature ≥ 1000 °C; Figure II.2.3)
2) Electronic balance (minimum displayed value: 0.1 mg)
3) Ultrapure water production system
4) Dryer
5) Ultrasonic cleaner

(2) Instruments

1) Quartz tubes
   - Quartz outer tube (Figure II.2.4)
   - Quartz inner tube (Figure II.2.5)
2) Bubbler tube (Figure II.2.6)[*181]
3) Quartz Wool
4) Clamp
5) Beakers (500 mL and 5 L)
6) Water bath
7) Fluoroplastic tape
8) Spatulas and stainless steel spoons
9) Micro spatula
10) CB boat (or half-split quartz glass; 14 mm × 12 mm × 140 mm)
11) Snap tube (capacity: 26 mL)
12) Volumetric flask (100 mL)
13) Micropipettes (1 mL, 2 mL, and 10 mL)
14) Pipette tips (1 mL, 2 mL, and 10 mL)
15) Aluminum foil
16) Gas burner

[*181] JIS Standard G2 and ISO Standard P40 (pore size: 40–50 μm)

(3) Reagents

Reagent masses and volumes specified here are indicative of preparation ratios. Adjust quantities as needed at the time of preparation. Use reagents compliant with the JIS. When no standard is specified, use the highest available reagent grade.

1) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of ultrapure water.
2) Nitric acid[*182,*183,*184] (mass fraction: 60%–61% (~13 mol/L); density: 1.38 g/mL)
   - Nitric acid (1 + 13; 1 part nitric acid and 13 parts water)
3) Acetone[*183,*184,*185]
4) Ethanol[*183,*185]
5) TMAH solution[*183,*184,*185] (mass fraction: 25%)
6) Vanadium pentoxide[*183,*184,*186]
7) Ultrapure water (purified to a resistivity of 18 MΩ·cm or more[*187])
8) Gases
   - Oxygen gas (purity ≥ 99.999%)
   - City gas (propane gas)

[*182] Class III Substances under the Ordinance on the Prevention of Hazards due to Specified Chemical Substances (indicating a risk of acute toxicity in the event of significant release): Exposure control measures, such as installation of local exhaust ventilation systems, are necessary to minimize worker exposure.

[*183] Classified as a hazardous substance requiring labeling under the Industrial Safety and Health Act (indicating potential risks of danger or adverse health effects to workers). Mandatory requirements include hazard labeling, provision of safety data sheets, and implementation of risk assessments with appropriate mitigation measures, along with worker education and training.

[*184] 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.” Further, necessary measures must be implemented to prevent theft, loss, leakage, or other incidents.

[*185] Classified as a Category IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Following precautions are necessary: Open flames must be strictly avoided. Store and handle the material below its flash point. Ensure separate storage from Category I and Category V Hazardous Substances. Implement measures to avoid static electricity generation. When transferring to smaller containers, avoid filling to full capacity to prevent potential rupture due to thermal expansion.

[*186] Designated as a Class II Substance under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (materials associated with chronic health effects such as carcinogenicity but not classified as Class I Substances). Exposure reduction measures are necessary, including the installation of local exhaust ventilation systems.

[*187] This corresponds to the definition provided in JIS K 0211: 分析化学用語(基礎部門) (2013), definition No. 5218.

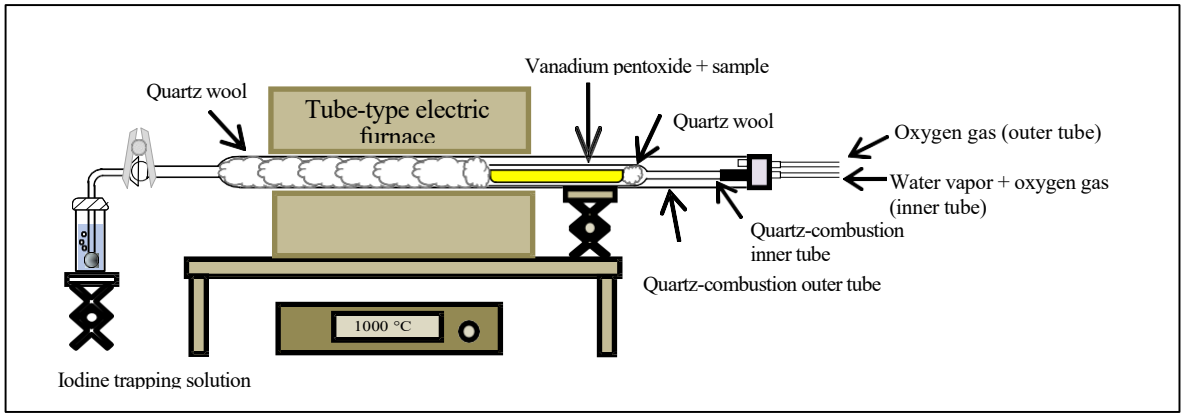



Figure II.2.2 Thermal hydrolysis analyzer

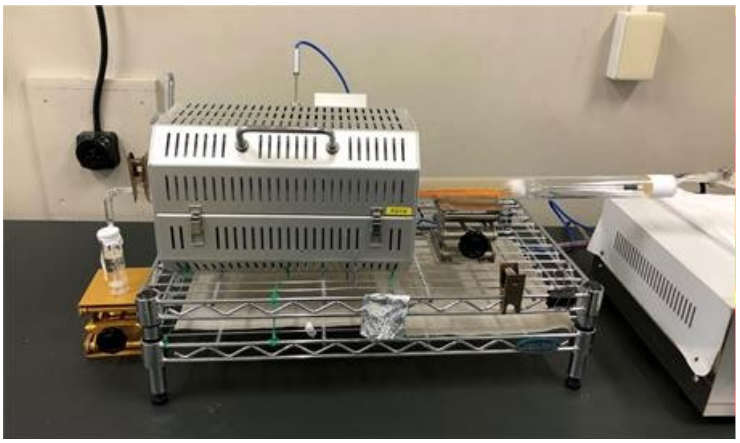


Figure II.2.3 Tube-type electric furnace

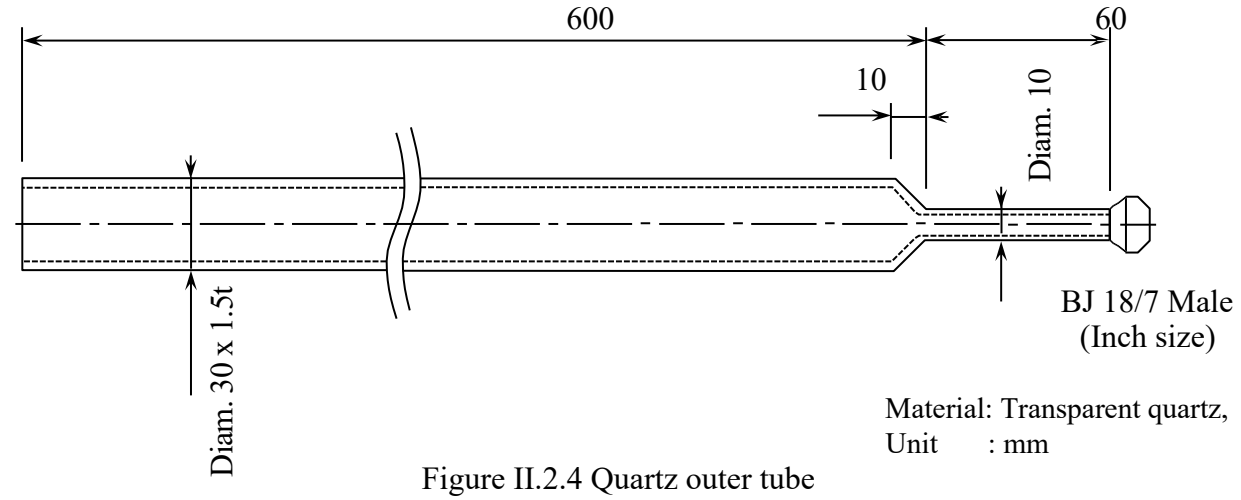



Figure II.2.4 Quartz outer tube

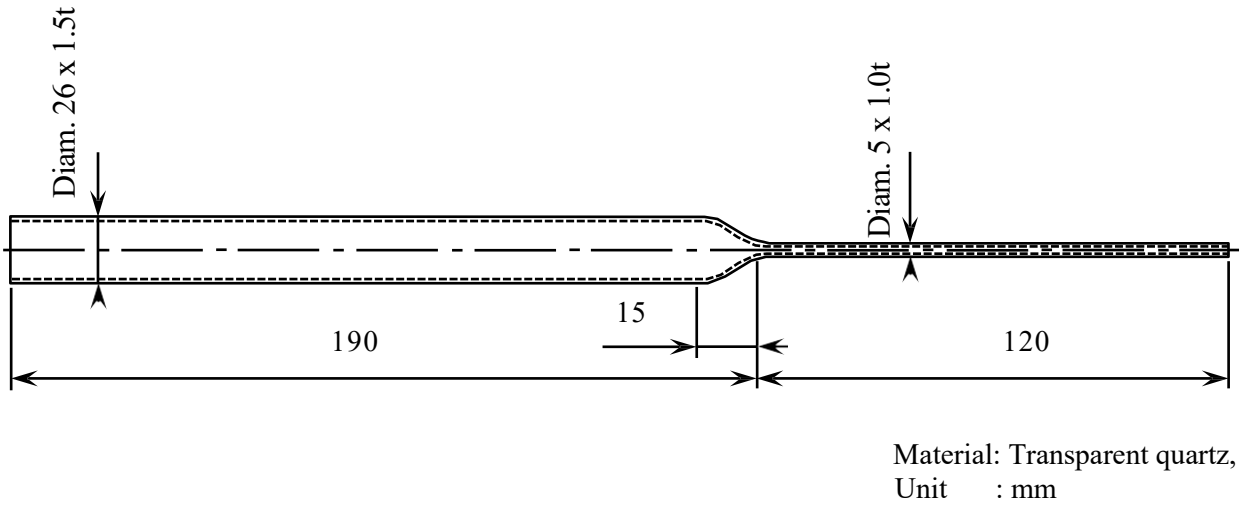



Figure II.2.5 Quartz inner tube

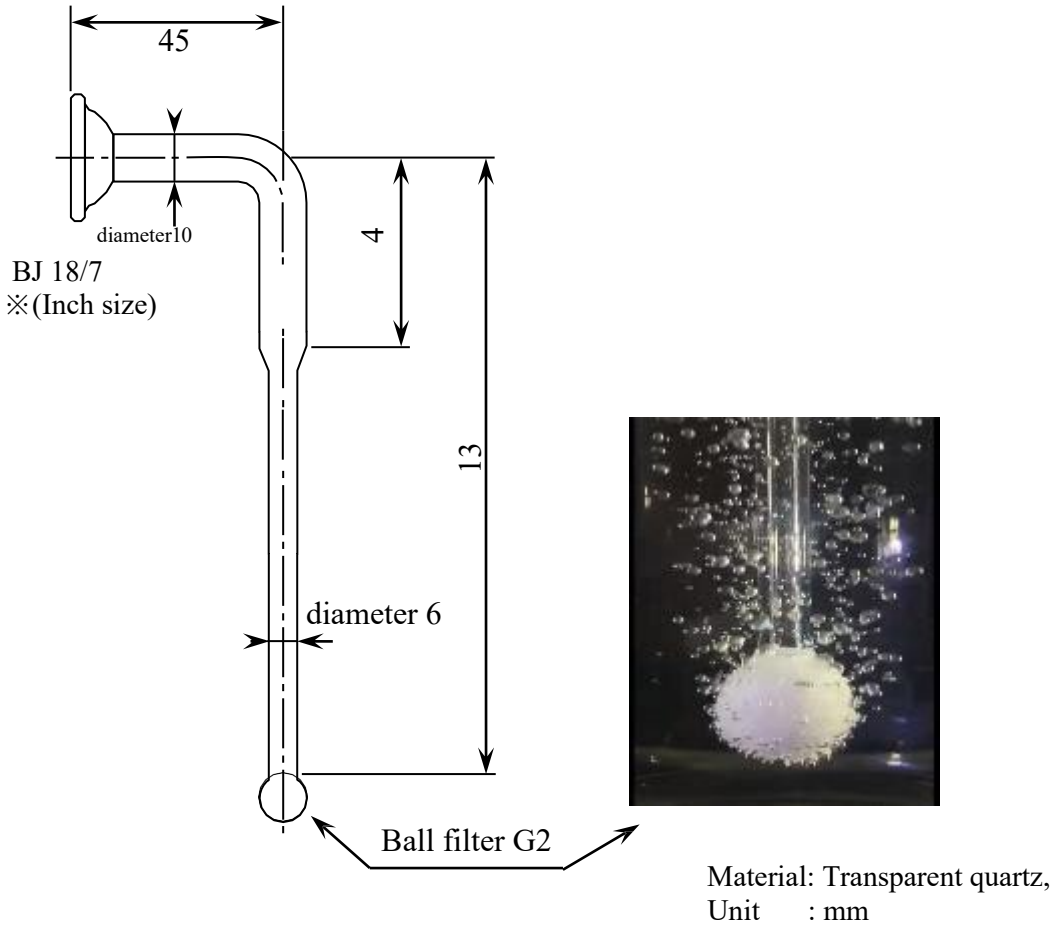



Figure II.2.6 Bubbler tube

## 2.2 Thermal Hydrolysis

### 2.2.1 Preparation

(1) Glassware

1) Wash glassware with acetone, ethanol, and pure water.
2) Place the glassware and nitric acid (1 + 13) in a 5-L beaker, cover with a watch glass, and heat on a gas burner until the solution boils.
3) Bring to boil and keep for 1 hour.
4) Stop heating and allow the solution to cool to room temperature.
5) Wash glassware with ultrapure water and dry in a dryer at 110 °C overnight[*188].

(2) CB boat (or half-split quartz glass)

1) Place the CB boat and ultrapure water in a 500 mL beaker and rinse using an ultrasonic cleaner for 30 minutes[*189].
2) Discard the ultrapure water in the beaker and repeat Step 1) three times.
3) Discard the ultrapure water in the beaker, add acetone, and rinse the beaker using an ultrasonic cleaner for 10 minutes.
4) Remove the CB boat using tweezers, place it in a washed 500 mL beaker, and dry at 80°C overnight.

(3) Blank firing of the quartz outer and inner tubes and the CB board

1) Fill the quartz outer and inner tubes with quartz wool.
2) Insert the CB boat into the inner tube, insert the inner tube in the quartz outer tube, align the outer tube with the right end of the CB boat, and the install the outer tube in the tube-type electric furnace[*190].
3) Connect the quartz outer and inner tubes to their respective oxygen supply lines. Then, set the oxygen flow rates to 11.0 mL/min for the inner tube and 12.0 mL/min for the outer tube.
4) Turn on the tube-type electric furnace, heat it to the set temperature of 1000°C, and maintain it in that state for 30 minutes.
5) Move the quartz outer tube approximately 10 cm to the right end[*191].
6) After confirming that the temperature of the tube-type electric furnace is 1000°C, maintain it in that state for 30 minutes.
7) Move the quartz outer tube again. Thus, blank fire the tube entirely by repeating Steps 5) and 6).

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[*188] To clean the volumetric flask, soak it in nitric acid (1 + 13) for 24 hours and then rinse with ultrapure water.
[*189] Since heat is generated inside the ultrasonic cleaner during cleaning, place ice water in the cleaner.
[*190] When closing the lid of the tube-type electric furnace, install the CB boat such that it is not visible.
[*191] In the case of combusting the outer tube shown in Figure II.2.4, the entire quartz outer tube must be moved 4–5 times to achieve complete blank firing.

8) Once the blank firing of the entire quartz outer tube is complete, switch off the tube-type electric furnace, close the oxygen gas line, and wait until the quartz outer tube has cooled to room temperature.

9) Cover both ends of the quartz outer tube with aluminum foil (with the CB boat still in the quartz inner tube).

### 2.2.2 Iodine Capture by Thermal Hydrolysis

(1) Preparation of an iodine-absorbing solution

1) Weigh the empty snap tube.

2) Using a micropipette, mix 8 mL of ultrapure water, 0.36 mL of the TMAH solution (25%), 1 mL of the sodium sulfite solution (10 w/v%), and then 8 mL of ultrapure water in a snap tube to obtain an $^{129}$I-absorbing solution.

(2) Weighing of samples and preparation for combustion

1) Weigh 1–2 g of vanadium pentoxide and place half of it in a CB boat.

2) Weigh the sample accurately and place it on top of the CB boat mentioned in Step 1).

3) Cover the sample in the CB boat mentioned in Step 2) with remaining vanadium pentoxide from Step 1). Thus, sandwich the sample between layers of vanadium pentoxide.

4) Place this CB boat in the quartz inner tube.

5) Apply grease to the sliding portion of the quartz outer tube, connect the bubbler tube and the quartz outer tube precisely, and fasten with a clamp.

6) Place the snap tube containing the iodine-absorbing solution prepared in "(1) Preparation of the iodine-absorbing solution" into the bubbler tube and cover with fluoroplastic tape.

7) Then, place the inner tube (with the CB boat) in the outer tube (connected with the bubbler tube).

8) Connect the inner and outer quartz tubes to the oxygen gas line and adjust the oxygen flow rate to 11.0 mL/min for the inner tube and 12.5 mL/min for the outer tube.

9) Confirm that bubbles are released from the bubbler tube mentioned in Step 6). If bubbles do not appear, check the connection points.

(3) Thermal hydrolysis

1) Switch on the water bath[*192]. Turn on the tube-type electric furnace, set the temperature of the furnace to 1000 °C, and heat the furnace.
2) When the temperature of the tube-type electric furnace reaches 1000 °C, move the outer tube into the electric furnace at a rate of 1 cm/3 min[*193] and thermally decompose the sample. Once the whole CB boat has been moved into the electric furnace, hold it there for 15 minutes[*194].
3) Move the outer tube present within the furnace toward its tip at a rate of 2 cm/1.5 min and heat it. Once moved toward the tip, hold it for ~5 minutes[*195].
4) Turn off the furnace and remove the bubbler tube and snap tube from the outer tube.
5) Using a paper rag wetted with acetone and ethanol, wipe off the grease applied to the outer and bubbler tubes[*196].
6) Using a micropipette, wash the inside and outside of the bubbler tube with 0.14 mL of the TMAH solution (25%) and 4 mL of ultrapure water in that order. Then, add the cleaning solution to the snap tube containing the iodine-absorbing solution.
7) Weigh the snap tube and calculate the weight of the iodine-absorbing solution.
8) Seal the snap tube containing the iodine-absorbing solution with fluoroplastic tape by wrapping it between the cap and the snap tube. Then, store the tube in a light-shielded container covered with aluminum foil.

## 2.3 Preparation of Measurement Samples

Dilute the iodine-absorbing solution using 0.5% TMAH to prepare a $^{129}$I measurement sample. Although the iodine-absorbing solution contains 0.6% TMAH, the effect of TMAH addition is considered negligible because the concentration of TMAH is reduced to 0.006% after 100-fold dilution.

1) Using a micropipette, take 1 g of the iodine-absorbing solution prepared in “2.2.2 Iodine Capture by Thermal Hydrolysis.”
2) Add it to a 100 mL volumetric flask.
3) Add 2 mL of the TMAH solution (25%).
4) Add ultrapure water up to the calibration mark of the volumetric flask.
5) Shake thoroughly and use as the sample for $^{129}$I measurement[*197].

[*192] When the ultrapure water in the water bath boils, switch off the water bath.
[*193] If the quartz outer tube is moved very quickly, the temperature inside the tube-type electric furnace may drop. Maintain the temperature in the electric furnace at 1000 °C at all times.
[*194] Ensure that vanadium pentoxide and the sample are completely molten before proceeding to Step 3).
[*195] Always check for air bubbles released from the bubbler tube during Steps 1), 2), and 3).
[*196] Take precautions to avoid burns from the quartz outer tube and bubbler tube with high temperatures.
[*197] When internal standards are added individually, adjust the addition amount so that the internal standard concentration is 10 μg/L.

# Chapter 3 Measurement

This chapter describes the entire analysis process: from sample preparation to measurement by triple quadrupole ICP–MS and calculation of $^{129}I$ radioactivity concentration. The main contents are as follows.

As a preparation step before the measurement, prepare calibration solutions.

During measurement, analyze the 0.5% TMAH solution prepared as described in Chapters 1 and 2 via triple quadrupole ICP–MS. Determination is performed using the internal-standard method with rhenium. In particular, the $^{129}I$ concentration is determined from the ratio of counting rates at *m/z* 129 and 185. $^{129}Xe$, which is present as an impurity in argon gas, is removed when using a collision/reaction cell (hereafter referred to as the "CRC") through a charge-transfer reaction with oxygen[*198]. Because it is essential to remove $^{129}Xe$ and maintain high sensitivity, the oxygen flow rate in the CRC should be evaluated in advance and optimized.

For the calculation of $^{129}I$ radioactivity concentration, apply $IH_2$ (ID) correction. The $IH_2$ (ID) correction requires the ratio of the amount of $^{127}I^1H_2$ ($^{127}I^2D$) to that of $^{127}I$ ($IH_2$ (ID) formation ratio).

Since there are few RMs with certified or reference values of $^{129}I$ radioactivity concentration detectable by this measurement method, it is necessary to validate the analytical process by the determination of $^{127}I$[*199].

## 3.1 Preparation of Calibration Solutions

### 3.1.1 Equipment, Instruments, and Reagents

(1) Equipment

1) Electronic balance (minimum displayed amount: 0.1 mg)
2) Ultrapure water production system

(2) Instruments

1) Micropipettes (0.2 mL, 1 mL, 2 mL, and 5 mL)
2) Pipette tips (0.2 mL, 1 mL, 2 mL, and 5 mL)
3) Volumetric flask (100 mL)

[*198] Through the charge-transfer reaction with oxygen ($Xe^+ + O_2 \rightarrow Xe + O^{2+}$), 129Xe loses its charge and is removed.
[*199] For the determination of $^{127}I$, refer to "Explanation B Determination of $^{127}I$."

(3) Reagents

Reagent masses and volumes specified here are indicative of preparation ratios. Adjust the quantities as needed at the time of preparation. Use reagents compliant with the JIS. When no standard is specified, use the highest available reagent grade.

1) TMAH solution[*200,*201,*202] (mass fraction: 25%)
2) Ultrapure water (purified to a resistivity of 18 MΩ·cm or more[*203])
3) $^{129}$I standard solution (40 Bq/g; 6 $\mu$g$^{129}$I/g)[*204,*205]

• $^{129}$I solution (2 Bq/L; 0.3 $\mu$g$^{129}$I/L) : Weigh 0.1 g of the $^{129}$I standard solution (40 Bq/g; 6 $\mu$g $^{129}$I/g) into a 100 mL volumetric flask, add 2 mL of the TMAH solution (25%), and dilute up to the calibration mark with ultrapure water. Add additional 5 g into a 100 mL volumetric flask, add 2 mL of the TMAH solution (25%), and add ultrapure water up to the calibration mark.

### 3.1.2 Preparation of $^{129}$I Calibration Solutions

1) Add 0.2, 0.5, 1, 2, and 4 mL of the $^{129}$I solution (2 Bq/L; 0.3 $\mu$g$^{129}$I/L) into 100 mL volumetric flasks[*206].
2) Add 2 mL of the 25% TMAH solution.
3) Add ultrapure water up to the calibration mark of the volumetric flask.
4) Shake thoroughly and use these as $^{129}$I calibration solutions (0.6, 1.5, 3, 6, and 12 ng

[*200] 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 about handling these substances.

[*201] 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.” Further, necessary measures must be undertaken to prevent theft, loss, leakage, or other incidents.

[*202] Classified as a Category IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Use of open flames is strictly prohibited. Store and handle the material below its flash point. Keep away from Category I and Category V Hazardous Materials. Take precautions to avoid static electricity generation. Avoid filling containers completely when repackaging to prevent rupture due to thermal expansion.

[*203] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

[*204] Iodine is highly volatile; hence, be careful to avoid contamination by $^{129}$I. Since the $^{129}$I standard solution has a very high $^{129}$I concentration, it is advisable to separate the laboratories that use the $^{129}$I standard solution from those that handle environmental samples.

[*205] The Act on the Regulation of Radioactive Isotopes and Related Substances applies. These substances require permission and notification for use, notification for business activities involving sale or rental, and permission for business activities involving disposal. The Nuclear Regulation Authority Notification No. 6 of March 18, 2020, entitled “To Determine the Quantity, etc. of Radioactive Isotopes” lists the lower limit quantities (notified quantities) for each nuclide. The ratio of each nuclide (Bq held/notified Bq) should be calculated for all nuclides held by the facility in use, and the sum of the ratios should not exceed “1.” In addition, the June 2005 Enforcement Order of the Act on the Regulation of Radioactive Isotopes and Related Substances introduced lower limit quantities for each nuclide. When the amount handled remains below these limits, use outside of a controlled area is permitted. For guidance on practical implementation, refer to the Safety Handling Manual for the Use of Unsealed Radioisotopes Below the Lower Limit Quantity published by the Japan Radioisotope Association (https://www.jrias.or.jp/report/cat1/308.html).

[*206] The concentration range specified for generating the calibration curve is provided as an example only. Actual calibration ranges should be set based on the instrument’s sensitivity and the expected sample concentrations.

$^{129}$I/L)*207,*208.

### 3.1.3 Example of an $^{129}$I Calibration Curve

A measurement example of a calibration solution prepared according to "3.1.2 Preparation of $^{129}$I Calibration Solutions" is provided below. In the example, rhenium was used as the internal-standard element. A calibration curve was prepared by plotting the counting rate ratio of *m/z* 129 and 185 on the vertical axis against the $^{129}$I concentration on the horizontal axis (Table II.3.1 and Figure II.3.1).

$^{129}$I standard solution: Commercially available product (41.7 ± 1 Bq/g)

Internal-standard element: Rhenium (introduced by online addition; ~10 $\mu$gRe/L)

Table II.3.1 Measurement of the $^{129}$I curve solution

| Calibration curve No. | $^{129}$I Concentration*1 (ng$^{129}$I/L) | *m/z* 129 (cps) | *m/z* 185 (cps) | Counting rate ratio |
|---|---|---|---|---|
| 1 | 0 | 0.10 | $5.30 \times 10^4$ | $1.89 \times 10^{-6}$ |
| 2 | 0.65 | 6.24 | $5.28 \times 10^4$ | $1.18 \times 10^{-4}$ |
| 3 | 1.63 | 16.14 | $5.22 \times 10^4$ | $3.09 \times 10^{-4}$ |
| 4 | 3.26 | 30.26 | $5.20 \times 10^4$ | $5.82 \times 10^{-4}$ |
| 5 | 6.52 | 61.04 | $5.21 \times 10^4$ | $1.17 \times 10^{-3}$ |
| 6 | 13.05 | 125.68 | $5.23 \times 10^4$ | $2.40 \times 10^{-3}$ |

*1 The specific radioactivity was set as $6.53 \times 10^6$ Bq/g, and the units were converted from the radioactivity concentration.

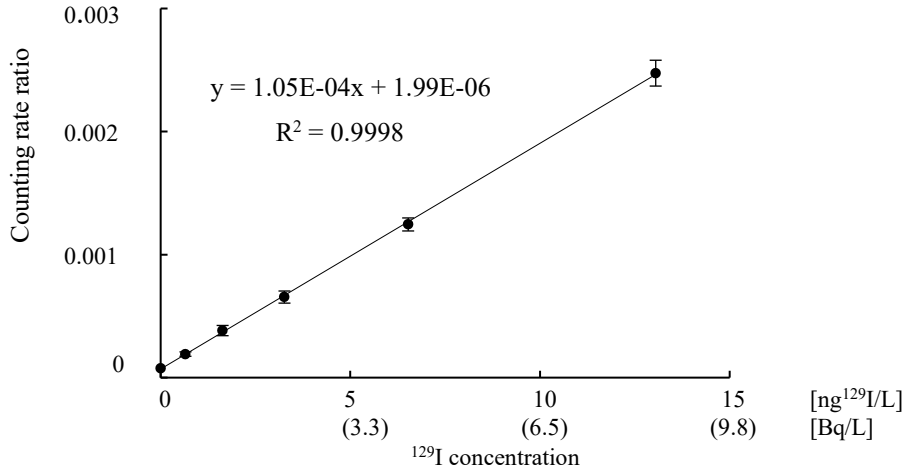



Figure II.3.1 Example of an $^{129}$I calibration curve

*207 In accordance with the units used in the instrument software, calibration curve values are expressed in terms of the mass concentration. If the standard solution is expressed in units of radioactivity, convert the values to mass concentration using the specific radioactivity.

*208 A 0.5% TMAH solution should be used as the blank (0 ng/L) for the calibration curve.

## 3.2 Measurement Operation

### 3.2.1 Equipment, Instruments, and Reagents

Reagent masses and volumes specified here are indicative of preparation ratios. Adjust the quantities as needed at the time of preparation. Use reagents compliant with the JIS. When no standard is specified, select the highest available reagent grade.

(1) Equipment

1) Triple quadrupole ICP–MS
2) Electronic balance (minimum displayed value: 0.1 mg)
3) Ultrapure water production system

(2) Instruments

1) Container for storing the measurement sample
2) Container for storing a cleaning solution
3) Connector for online addition[*209]

(3) Reagents

1) Nitric acid[*210,*211,*212] (mass fraction: 60%–61% (~13 mol/L); density: 1.38 g/mL; used for the determination of toxic metals)

   • 2% nitric acid (1 + 29) (0.4 mol/L nitric acid and water): Add 1 part of nitric acid with 29 parts of water and mix

2) TMAH solution[*211,*212,*213] (mass fraction: 25%) 0.5% TMAH solution: Dilute 20 mL of the 25% TMAH solution with ultrapure water so that the total volume is 1000 mL
3) Tuning solution[*211,*214]
4) Potassium iodide[*211,*215] ($^{129}I/^{127}I$ isotopic ratio of less than $10^{-10}$)

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[*209] This is not necessary when internal standards are added separately to the measurement sample.

[*210] Class III Substances in the Ordinance on Prevention of Hazards due to Specified Chemical Substances (substances that cause acute poisoning due to large volume leakage): It is necessary to take measures to reduce exposure concentrations, such as installing local exhaust ventilation systems.

[*211] 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 about handling these substances.

[*212] 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." Further, necessary measures must be taken to prevent theft, loss, leakage, and similar incidents.

[*213] Classified as a Class IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Following precautions are necessary: Open flames must be strictly avoided. Store and handle the material below its flash point. Ensure storage separate from Category I and Category V Hazardous Substances. Implement measures to avoid static electricity generation. When transferring to smaller containers, avoid filling to full capacity to prevent potential rupture due to thermal expansion.

[*214] Used to tune instruments. This is usually a solution of lithium, yttrium, cerium, or thallium (approximately 1 μg/L).

[*215] Store in a cool, dark place. Depending on storage conditions, some iodine may be released; hence, long-term storage should be avoided.

- $^{127}$I solution (10 mgI/mL): Dry ~3 g of potassium iodide at 110 °C for 3 hours and cool in a desiccator for one hour. Dissolve 1.308 g in ultrapure water, add 2.3 g of sodium sulfite, transfer to a 100 mL volumetric flask, and add ultrapure water up to the calibration mark.
- $^{127}$I solution (100 $\mu$gI/L): Add 0.1 mL of the $^{127}$I solution (10 mgI/mL) into a 100 mL volumetric flask and add ultrapure water up to the calibration mark. Next, add 1 mL into a 100 mL volumetric flask, add 2 mL of the 25% TMAH solution, and add ultrapure water up to the calibration mark.
- $^{127}$I solution (10 $\mu$gI/L): Add 10 mL of the $^{127}$I solution (100 $\mu$gI/L) into a 100 mL volumetric flask, add 2 mL of the 25% TMAH solution, and add ultrapure water up to the calibration mark.

5) Rhenium standard solution (1000 mgRe/L)[*210,*211] (commercially available product)
   - Rhenium internal-standard solution (100 µgRe/L): Add 1 mL of the rhenium standard solution (1000 mgRe/L) into a 100 mL volumetric flask and add ultrapure water up to the calibration mark. Next, add 1 mL into a 100 mL volumetric flask, add 2 mL of the 25% TMAH solution, and add ultrapure water up to the calibration mark.
6) Ultrapure water (purified to a resistivity of 18 MΩ·cm or more[*216])
7) Gases
   - Argon gas (purity ≥ 99.99%)
   - Oxygen gas (purity ≥ 99.999%)

### 3.2.2 Premeasurement Checks

Perform the following checks. For detailed information and procedures, refer to the equipment manufacturer's instructions.

(1) Check CRC gas purging

(2) Check feeding system parts

(3) Connect the connector for online addition[*217] (Figure II.3.2)

[*216] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

[*217] This is not necessary when internal standards are added to the measurement sample separately.

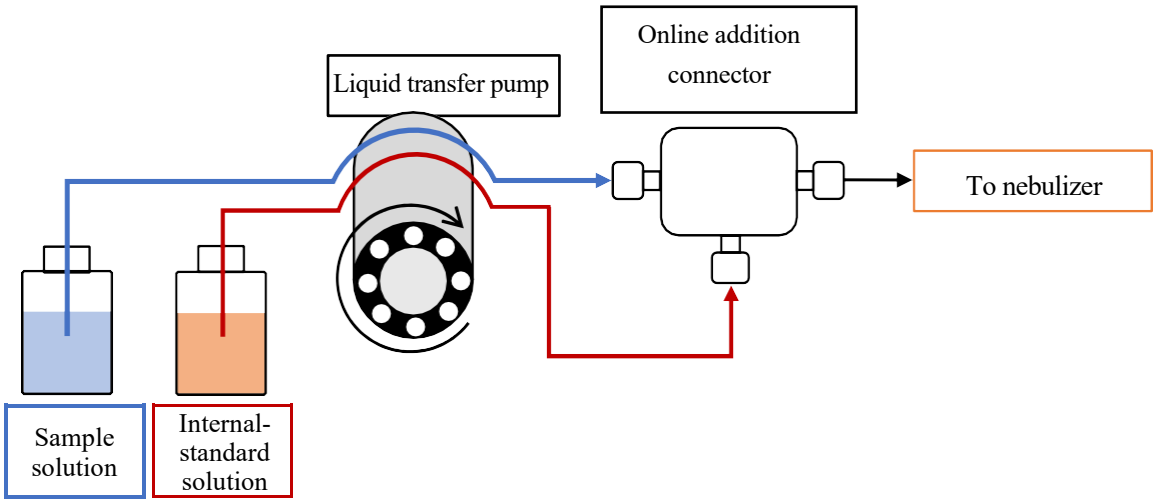



Figure II.3.2 Schematic of the online addition of the internal standard

(4) Check the remaining argon gas level

(5) Check the coolant

(6) Check the exhaust system

### 3.2.3 Instrument Start-up

Methods for aspirating measurement samples include suction using a liquid transfer pump (manual or autosampler suction) and negative-pressure suction. Negative-pressure suction does not require a liquid transfer pump, eliminating flow pulsation and resulting in a more stable detector signal. However, it is unsuitable for highly viscous samples, and the measured sample must be changed manually. In the context of this document, aspiration using an autosampler is considered, which is common in routine analysis.

1) Open the argon gas valve.
2) Turn on the cooling water circulator and exhaust system.
3) Open the oxygen gas valve[*218].
4) Attach the sample tube and drain tube to the liquid transfer pump.
5) Turn on the autosampler.
6) Add the cleaning solution (2% nitric acid and ultrapure water).
7) Ignite the plasma.
8) While introducing 2% nitric acid and ultrapure water, wait ~10 minutes until the plasma stabilizes[*219].

[*218] Additionally, supply helium gas as needed, such as during the measurement of $^{127}I$.
[*219] Verify that the interface pressure, analyzer pressure, and carrier-gas flow rate remain unchanged from the values recorded at the most recent plasma ignition.

### 3.2.4 Instrument Adjustment

Adjust the instruments after each start-up because the optimal parameters change every day.

1) Perform sensitivity and mass-axis adjustment using the tuning solution[*220,*221]. Further, check the short-term stability[*221] and device background[*222].
2) Use the tuning solution to adjust sensitivity for each gas type. Adjust the oxygen gas flow after setting the optimal flow rate[*223].
3) $^{127}$I Use the $^{127}$I solution (100 $\mu$gI/L) to adjust the PA factor[*224].
4) After introducing ultrapure water, add 2% nitric acid to clean the sample introducing system.
5) After introducing ultrapure water for ~15 minutes, add the 0.5% TMAH solution.
6) Introduce the $^{127}$I solution (10 $\mu$gI/L).
7) Adjust parameters to a sufficiently low background at *m/z* 129 and a sufficiently high counting rate at *m/z* 127[*225,*226].
8) Introduce the 0.5% TMAH solution and clean the sample introduction system.

### 3.2.5 Iodine Determination

Iodine exhibits a significant memory effect; therefore, the sequence of measurements must be carefully controlled to prevent cross-contamination and carry-over between samples[*227]. When the approximate concentration of the samples is known, it is recommended to measure samples in order of increasing concentration, starting with the lowest, to minimize memory effects and ensure accurate determination.

To minimize the impact of iodine memory effects in this measurement method, a 0.5% TMAH solution is measured both before and after each sample. The background signal obtained from these measurements is then subtracted from the sample's counting rate to correct for memory contributions.

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[*220] This adjustment determines the sensitivity (lower detection limit, etc.).
[*221] If the short-time stability is >5%, tighten the liquid transfer pump appropriately.
[*222] If the background level is elevated, clean the flow path by introducing a cleaning solution.
[*223] The optimal gas flow rate should be reviewed in advance according to "3.3 Optimization of the Oxygen Gas Flow Rate."
[*224] Adjust the sensitivity difference between P (pulse-counting measurement) and A (analog measurement). This may be done during sample measurement. Particular attention is required when determining the $IH_2$ (ID) formation ratio, in which *m/z* 129 is measured in the pulse mode and m/z 127 is measured in the analog mode; therefore, sensitivity matching shall be performed prior to applying the $IH_2$ (ID) correction.
[*225] Ideally, adjustment should be performed using the SB ratio (signal-to-background counting rate ratio) of the target analyte element $^{129}$I. However, because the $^{129}$I standard solution is valuable, the $^{127}$I solution is used instead.
[*226] See "Explanation C Example of Measurement Parameters" for parameter examples.
[*227] When quantifying $^{127}$I, $^{127}$I and $^{129}$I should be measured separately because the dilution factors of measurement samples are different. The order of measurement should be $^{127}$I and then$^{129}$I. Since $^{129}$I measurement samples have lower dilution factors and a high concentration of $^{127}$I is simultaneously introduced into the instrument during measurement, when measuring $^{127}$I after $^{129}$I, prolonged rinsing or cleaning of the sample introduction parts is required.

(1) Preparation for the measurement method

1) Set the *m/z* value to be measured, integration time, number of repetitions, and other conditions[*228]. The target *m/z* values are 127, 129, and 185[*229].
2) Set the rinse time[*230].
3) Register the information pertaining to calibration solutions and measurement samples as well as the measurement order in the autosampler. Additionally, specify the positions of the measurement samples and configure the measurement sequence so that each sample is measured alternately with a 0.5% TMAH cleaning solution to mitigate memory effects.

(2) Determination

1) Transfer the calibration solutions and measurement samples into the measurement container.
2) Place the samples into the autosampler at the positions defined in the measurement method.
3) Introduce the rhenium internal-standard solution (100 $\mu$gRe/L) via online addition, and verify the stability of the signal before proceeding with sample measurement.
4) Measure the 0.5% TMAH solution as a calibration blank solution and then the calibration solution. Next, determine the counting rate ratio at *m/z* 129 and 185. Subsequently, create a calibration curve relating the $^{129}$I concentration to the counting rate ratio.
5) Measure the sample solution. Then, using the counting rate ratio at *m/z* 129 and 185 together with the calibration curve, calculate the $^{129}$I concentration (ng/L).

### 3.2.6 Measurement Precautions

For accurate and reliable measurements, ensure adherence to the following points.

(1) Confirmation of procedural blanks

If the procedural blank exhibits a high counting rate while the calibration blank remains within acceptable limits, contamination introduced during the analytical process should be suspected and investigated. Depending on the degree of contamination, address possible causes and repeat the analysis.

(2) Confirmation of spectral interference

Confirm that the counting rates of molybdenum and cadmium are sufficiently low for each sample to be measured[*231].

(3) Confirmation of the memory effect

[*228] See "Explanation C Example of Measurement Parameters" for parameter examples.
[*229] Measure *m/z* 127 at the same time as *m/z* 129 to determine if $IH_2$ (ID) correction is possible.
[*230] Because iodine exhibits a pronounced memory effect, sufficient rinsing between measurements is essential to eliminate carry-over and ensure accurate results. It is advisable to determine the required cleaning time in advance.
[*231] It is advisable to determine the allowable upper limit of the counting rate in advance. For details, refer to "A.1 Spectral Interference" in "Explanation A Interference Factors in Triple Quadrupole ICP–MS."

Measure a 0.5% TMAH rinse solution or calibration blank solution before and after sample measurement to confirm the memory effect. If rinsing is insufficient, take countermeasures such as extending the rinsing time or increasing the concentration of the rinse solution.

(4) Variations in internal-standard counting rates

To monitor for nonspectral interferences and instrument drift over time, verify that the internal-standard counting rate of each sample does not deviate significantly from that of the calibration blank. For details, refer to JIS K 0133[*232].

### 3.2.7 Completion of measurement

1) After introducing the 0.5% TMAH solution for at least 15 minutes, introduce ultrapure water for 15 minutes to rinse the flow path.
2) Turn off the plasma.
3) If contamination is observed on the sample introduction parts or if the instrument background level has increased, remove the parts and clean them[*233].

## 3.3 Optimization of the Oxygen Gas Flow Rate

The ideal oxygen gas flow rate is one at which $^{129}Xe$ is sufficiently removed, the sensitivity for $^{129}I$ is high, and the $IH_2$ (ID) formation ratio is low. Therefore, the optimization of the oxygen gas flow rate should be considered. Although it is preferable to evaluate the $IH_2$ (ID) formation ratio using $^{127}I^1H_2$ ($^{127}I^2D$), this would require the introduction of very high concentrations of $^{127}I$ and would result in significant memory effects. Therefore, the evaluation is performed using the monohydride formation ratio based on $^{127}I^1H$ (hereinafter referred to as the "IH formation ratio"). Measure *m/z* 127, 128, and 129 in seawater or seaweed samples while systematically varying the oxygen gas flow rate. Select the flow rate that provides adequate sensitivity at *m/z* 127, while maintaining the background signal at *m/z* 129 and the IH formation ratio—defined as the counting rate ratio of *m/z* 128 to 127—at sufficiently low levels.

Using samples with a high $^{127}I$ concentration, measure *m/z* 127 and 128 to confirm the $^{127}I$ sensitivity and the IH formation ratio in the sample matrix. In addition, using samples with a low $^{127}I$ concentration, measure *m/z* 129 to confirm the removal of $^{129}Xe$ under conditions where $^{127}I^1H_2$ ($^{127}I^2D$) does not interfere.

For an example of the evaluation of the oxygen gas flow rate, refer to "Explanation C Example of Measurement Parameters."

[*232] JIS K 0133: 誘導結合プラズマ質量分析通則 (2022)

[*233] For detailed cleaning instructions, refer to the instrument manufacturer's guide.

### 3.3.1 Equipment, Instruments, and Reagents

The following instruments and reagents are required. In addition, other instruments and reagents necessary for measurements described in "3.2.1 Equipment, Instruments, and Reagents" in "3.2 Measurement Operation" are required.

(1) Equipment

1) Balance (minimum readability: 1 mg)
2) Ultrapure water production system

(2) Instruments

1) Volumetric flask (100 mL)
2) Micropipettes (1 mL and 10 mL)
3) Pipette tips (1 mL and 10 mL)

(3) Reagents

1) $^{127}$I solution (10 mgI/mL; prepare as per Section 3.2.1)

・ $^{127}$I solution (10 mgI/L): Add 0.1 mL of the $^{127}$I solution (10 mgI/mL) into a 100 mL volumetric flask, add 2 mL of the 25% TMAH solution, and add ultrapure water up to the calibration mark.

2) TMAH solution[*234,*235,*236] (mass fraction: 25%)

・ 0.5% TMAH solution: Dilute 20 mL of the 25% TMAH solution with ultrapure water so that the total volume is 1000 mL.

3) Ultrapure water (purified to a resistivity of 18 MΩ·cm or higher[*237])

### 3.3.2 Operation

(1) Preparation of measurement samples

1) Prepare samples for $^{129}$I measurement as described in "Chapter 1 Seawater Samples" for seawater and "Chapter 2 Seaweed Samples" for seaweeds. Use them as $^{129}$I confirmation samples.

[*234] 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 about handling these substances.

[*235] 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." Further, necessary measures must be taken to prevent theft, loss, leakage, and similar incidents.

[*236] Classified as a Category IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Use of open flames is strictly prohibited. Store and handle below the flash point. Keep away from Category I and Category V Hazardous Materials. Avoid static electricity generation. Avoid filling containers completely when repackaging to prevent rupture due to thermal expansion.

[*237] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

2) Add 1 mL of the $^{127}$I standard solution (10 mg I/L) to 9 mL of the $^{129}$I measurement sample to prepare a solution with a final iodine concentration of 1 mg/L. Use this solution as the $^{127}$I and $^{128}$I measurement samples.

(2) Measurement operation

1) Vary the oxygen gas flow rate from 0 mL/min to the maximum setting in increments of approximately 0.05 mL/min, and measure *m/z* 129 for both the $^{129}$I confirmation sample and the 0.5% TMAH blank solution at each setting.
2) In the same manner, measure *m/z* 127 and 128 for the $^{127}$I and $^{128}$I measurement samples and the 0.5% TMAH blank solution.
3) Determine the oxygen gas flow rate at which the $^{127}$I sensitivity is high and the *m/z* 129 counting rate and the counting rate ratio of *m/z* 128 to 127 (IH formation ratio) are sufficiently low. (See "Explanation C Example of Measurement Parameters" for a detailed evaluation example.)

## 3.4 Confirmation of the Dihydride Formation Ratio

For $IH_2$ (ID) correction, it is necessary to determine the $IH_2$ (ID) formation ratio in advance. In this measurement method, the $IH_2$ (ID) formation ratio is defined as follows.

[$IH_2$ (ID) formation ratio] = [$m/z$ 129 net counting rate] / [$m/z$ 127 counting rate]

The $IH_2$ (ID) formation ratio is determined by measuring a $^{127}$I solution at a concentration of several hundred ppm. The resulting net counting rate at *m/z* 129 is attributed to $^{127}I^1H_2$ ($^{127}I^2D$) formation and is divided by the counting rate at *m/z* 127. Because a very high-concentration iodine solution is introduced into the instrument, the memory effect[*238] is significant. Avoid measuring normal samples after measuring the $IH_2$ (ID) formation ratio. Instead, always remove and clean the introduction system.

Since the $IH_2$ (ID) formation ratio varies from day to day[*239], it is recommended to measure it periodically.

### 3.4.1 Equipment, Instruments, and Reagents

The following instruments and reagents are required. In addition, instruments necessary for measurements described in "3.2.1 Equipment, Instruments, and Reagents" in "3.2 Measurement Operation" are required.

(1) Equipment

1) Ultrapure water production system

[*238] Iodine is known to exhibit a pronounced memory effect, whereby residues from previously measured samples persist within the instrument and contribute to subsequent signals.
[*239] For daily fluctuations, refer to "A.1.1 $^{127}$I Hydrides" in "Explanation A Interference Factors in Triple Quadrupole ICP–MS."

(2) Instruments

1) Micropipettes (2 mL and 5 mL)

2) Pipette tips (2 mL and 5 mL)

3) 100 mL containers (volumetric flasks, polyethylene vessels, centrifuge tubes, etc.)

(3) Reagents

1) $^{127}$I solution (prepare as per Section 3.2.1)

- $^{127}$I solution (10 mgI/mL)
- $^{127}$I solution (100 $\mu$gI/L)

2) TMAH solution[*240,*241,*242] (mass fraction: 25%)

3) Ultrapure water (purified to resistivity of 18 MΩ·cm or higher[*243])

### 3.4.2 Preparation of Measurement Samples

In the context of this document, a $^{127}$I solution (400 mgI/L) is used as the sample for hydride confirmation. Although a lower concentration can be used due to the reduced memory effect from $^{127}$I, care must be taken regarding the increase in the counting error associated with a decrease in the *m/z* 129 counting rate[*244]. If a concentration of >400 mgI/L is used, attention should be paid not only to the memory effect but also to whether the instrument's counting upper limit[*245] is exceeded.

1) Add 4 mL of the $^{127}$I solution (10 mgI/mL) into a 100 mL container.

2) Add 2 mL of the 25% TMAH solution.

3) Add 100 mL of ultrapure water to obtain a hydride confirmation sample (400 mgI/L).

[*240] 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 about handling these substances.

[*241] 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." Further, necessary measures must be taken to prevent theft, loss, leakage, and similar incidents.

[*242] Classified as a Class IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Following precautions are necessary: Open flames must be strictly avoided. Store and handle the material below its flash point. Ensure separate storage from Category I and Category V Hazardous Substances. Implement measures to avoid static electricity. When transferring to smaller containers, avoid filling them to full capacity to prevent potential rupture due to thermal expansion.

[*243] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

[*244] For variations in $^{127}$I concentration ranges, refer to "A.1.1 $^{127}$I Hydrides" in "Explanation A" Interference Factors in Triple Quadrupole ICP–MS."

[*245] The upper counting limit in a typical triple quadrupole ICP–MS device is $5 \times 10^9$ to $8 \times 10^{10}$ cps in analog measurements. When the sensitivity is 10000 cps per 1 µg/L of $^{127}$I, a 1000 mgI/L solution of $^{127}$I corresponds to $1 \times 10^{10}$ cps.

### 3.4.3 Measurement

1) Turn on the triple quadrupole ICP–MS device and adjust the instrument as described in "3.2 Measurement Operation" (from "3.2.2 Premeasurement Checks" to "3.2.4 Instrument Adjustment").
2) Use the $^{127}$I solution (100 $\mu$gI/L) to adjust the PA factor[*246].
3) Measure the hydride confirmation sample (400 mg I/L), and measure the blank sample (0.5% TMAH solution) both before and after the sample measurement. While the measurement parameters should be the same as those used for $^{129}$I measurement, the integration time should be 0.1 s for *m/z* 127 and 10 s for *m/z* 129[*247].
4) After completion of measurements, remove and clean the components of the sample introduction system[*248].

### 3.4.4 Calculation

When calculating the $IH_2$ (ID) formation ratio, the standard deviation should also be calculated as it is used to determine whether to apply the $IH_2$ (ID) correction (refer to Section 3.5.2).

(1) Subtract the average of the pre and postmeasurement blank signals to obtain the net counting rate at m/z 129 for the hydride confirmation sample. The standard deviation of the counting rate is that obtained from five repeated measurements.

$$r_{129n} \pm \sigma_{129n} = r_{129} - (r_{129b1} + r_{129b2})/2 \pm \sqrt{\sigma_{129}{}^2 + (\frac{\sigma_{129b1}}{2})^2 + (\frac{\sigma_{129b2}}{2})^2}$$

$r^{129}$n and $\sigma^{129}$n : Net counting rate and standard deviation at *m/z* 129 of the sample (cps)

$r^{129}$ and $\sigma^{129}$ : Counting rate and standard deviation at *m/z* 129 of the sample (cps)

$r^{129b1}$ and $\sigma^{129b1}$ :Counting rate and standard deviation at m/z 129 of the premeasurement blank (cps)

$r^{129b2}$ and $\sigma^{129b2}$ :Counting rate and standard deviation at *m/z* 129 of the postmeasurement blank (cps)

[*246] Adjust the sensitivity difference between the P (pulse mode) and A (analog mode) measurements. If $^{127}$I is not being quantified, this step may be omitted. However, the measurement conditions should be identical to those for $^{129}$I.

[*247] Since a very high-concentration iodine solution is being introduced, the measurement duration should be kept short. Additionally, measurements of other elements should not be performed during this period.

[*248] If contamination persists after cleaning glass components by soaking in dilute nitric acid, it is recommended to immerse the components in the 0.5% TMAH solution for several hours to overnight, followed by rinsing with ultrapure water, and then soaking again in dilute nitric acid.

(2) Divide by the counting rate at m/z 127 to obtain the $IH_2$ (ID) formation ratio.

$$H2 \pm \sigma_{H2} = r_{129n}/r_{127} \pm r_{129n}/r_{127} \times \sqrt{(\frac{\sigma_{129n}}{r_{129n}})^2 + (\frac{\sigma_{127}}{r_{127}})^2}$$

$H2$ and $\sigma_{H2}$ : $IH_2$ (ID) formation ratio and standard deviation

$r_{127}$ and $\sigma_{127}$ : Counting rate and standard deviation at *m/z* 127 of the sample (cps)

## 3.5 Calculation of $^{129}I$ Radioactivity Concentration

### 3.5.1 Calculation of $^{129}I$ radioactivity concentration

The $^{129}I$ radioactivity concentration is calculated by first determining the iodine concentration in the sample after applying the $IH_2$ (ID) correction, and then converting this value from specific activity to radioactivity concentration. For seawater samples with low $^{127}I$ concentrations, the $IH_2$ (ID) correction may be omitted; however, for seaweed samples, it is desirable to perform the correction. When performing the correction, calculate the $^{129}I/^{127}I$ isotopic ratio of the sample and confirm that the ratio falls within a range for which the correction is valid. The analytical procedure assumes 100% recovery, and no recovery rate correction is performed.

(1) $IH_2$ (ID) correction

From the *m/z* 127 counting rate of the sample and the $IH_2$ (ID) formation ratio[*249], calculate the counting rate of $^{127}I^1H_2$ ($^{127}I^2D$).

$$r_{H2} = r_{127} \times H_2$$

$r_{H2}$ : Counting rate of $^{127}I^1H_2$ ($^{127}I^2D$) (cps)

$r_{127}$ : Counting rate at *m/z* 127 of the measured sample (cps)

$H2$ : $IH_2$ (ID) formation ratio

(2) Net counting rate

Subtract the blank counting rate and the counting rate of $^{127}I^1H_2$ ($^{127}I^2D$) from the counting rate at *m/z* 129 of the sample to obtain the net counting rate. Because iodine is highly affected by the memory effect, the average of the premeasurement and postmeasurement counting rates of blanks are subtracted in this measurement method[*250].

[*249] Determined according to "3.4 Confirmation of the Dihydride Formation Ratio."

[*250] It is possible to evaluate which blank contributes more significantly to the signal and select the appropriate blank for subtraction. The types of blanks and the effects they are intended to correct are summarized below: Calibration blank: Accounts for the instrument's background signal;
Procedural blank: Accounts for contamination introduced during the analytical procedure;
Pre- and postmeasurement blanks: Account for carry-over (memory effects) from previously measured samples.

$$r_{129n} = r_{129} - (r_{129b1} + r_{129b2})/2 - r_{H2}$$

$r_{129n}$ : Net counting rate at *m/z* 129 (cps)

$r_{129}$ : Counting rate at m/z 129 of the measured sample (cps)

$r_{129b1}$ : Counting rate at m/z 129 of the premeasurement blank (cps)

$r_{129b2}$ : Counting rate at m/z 129 of the postmeasurement blank (cps)

(3) $^{129}$I concentration in the measured sample

The $^{129}$I concentration in the measured sample is calculated from the slope and intercept of the calibration curve and the internal-standard counting rate.

$$C_s = \frac{r_{129n}/r_{is} - b}{a}$$

$C_s$ : Concentration of the measurement sample (ng/L)

$r_{is}$ : Counting rate of the internal standard (cps)

$a$ : Slope of the calibration curve (cps/(ng/L))

$b$ : Intercept of the calibration curve

(4) $^{129}$I concentration in the sample

The $^{129}$I concentration in the sample is calculated from the dilution factor and the sample volume.

1) Seawater samples

Calculate the $^{129}$I concentration in the sample according to the following equation:

$$C_{sp} = \frac{C_s \times V}{W_s}$$

$C_{sp}$ : Sample concentration (ng/L)

$V$ : Capacity of the volumetric flask (mL)

$W_s$ : Sample volume (mL)

2) Seaweed samples

Calculate the $^{129}$I concentration in the sample according to the following equation:

$$C_{sp} = \frac{C_s \times Z \times w \times D}{m \times 100}$$

$C_{sp}$ : Sample concentration (ng/kg, raw)

$Z$ : Dry residue (%)

$w$ : Weight of the trapping solution (g)

$D$ : Dilution factor

$W_s$ : Sample weight (g; dry matter)

(5) Calculation of the radioactivity concentration

The $^{129}$I radioactivity concentration in the sample is calculated according to the following equation:

$$A = C_{sp} \times S \times 10^{-9}$$

$A$ : $^{129}$I radioactivity concentration in the sample (Bq/L or Bq/kg; raw sample)

$S$ : Specific radioactivity (Bq/g)

$$S = \frac{\ln 2 \times N_A}{T \times A_r}$$

$N_A$ : Avogadro's number (mol$^{-1}$)

$T$ : Half-life of $^{129}$I (s)

$A_r$ : Atomic weight of $^{129}$I

### 3.5.2 Determination of Correction Applicability

Spectral interference correction methods such as the $IH_2$ (ID) correction should be applied only when the corrected results can be considered reliable. It is advisable to establish criteria for applicability in advance.

JIS K 0102*[251] states, with regard to the applicable range of spectral interference correction, that "for samples in which the correction amount exceeds 50% of the original measured value, accuracy decreases, and therefore, methods using correction equations cannot be applied." If this statement is directly applied to the $^{129}$I/$^{127}$I isotopic ratio, the correction method cannot be applied when the isotopic ratio of the sample is less than the $IH_2$ (ID) formation ratio*[252].

However, in this iodine measurement method, measurement variability is taken into account, and the sum of the $IH_2$ (ID) formation ratio and the standard deviation of the counting rate is used as the criterion (hereinafter referred to as the "correction applicability criterion"). When the isotopic ratio of the sample is less than this correction applicability criterion, the $IH_2$ (ID) correction cannot be applied.

*251 JIS K 0102: 工場排水試験方法 (2016)

*252 When the allowable correction value specified in JIS K 0102 is expressed mathematically and applied to the $IH_2$ (ID) correction, it is given by the following equation:
0.5 = [correction amount]/([correction amount] + [amount in the sample])
→ 0.5 = [$^{127}$I$^{1}$H$_2$ ($^{127}$I $^{2}$D) amount]/([$^{127}$I $^{1}$H$_2$ ($^{127}$I $^{2}$D) amount] + [amount of $^{129}$I in the sample])
When applied to the $^{129}$I/$^{127}$I isotopic ratio and rearranged, the expression becomes
0.5 = [$IH_2$ (ID) formation ratio]/([$IH_2$ (ID) formation ratio] + [isotopic ratio of the sample]).
We thus obtain [isotopic ratio of sample] = [$IH_2$ (ID) formation ratio].

(1) Calculation of the correction applicability criterion

The correction applicability criterion is calculated according to the following equation:

$L = H2 + \sigma_{H2}$.

$L$ : Correction applicability criterion

$H2$ and $\sigma_{H2}$ : $IH_2$ (ID) formation ratio and standard deviation

(2) Confirmation of the isotopic ratio

The isotopic ratio of the sample is calculated according to the following equations:

$r_{127n} = r_{127} - (r_{127b1} + r_{127b2})/2$,

$r_{127n}$: Net counting rate at *m/z* 127 (cps)

$r_{127b1}$: Counting rate at *m/z* 127 of the premeasurement blank (cps)

$r_{127b2}$: Counting rate at *m/z* 127 of the postmeasurement blank (cps)

$R_{129/127} = r_{129n}/r_{127n}$

$R_{129/127}$ : $^{129}I/^{127}I$ isotopic ratio of the sample

$r_{129n}$ : Net counting rate at *m/z* 129 (cps)

(3) Determination of correction applicability

Only when the $^{129}I/^{127}I$ isotopic ratio of the sample is equal to or greater than the correction applicability criterion may the correction method described in "3.5.1 Calculation of $^{129}I$ Radioactivity Concentration" (in "(1) $IH_2$ (ID) correction") be applied. Note that the isotopic ratio of the sample obtained here has not been corrected for the mass discrimination effect[*253]. Therefore, this uncertainty may be large.

(4) Detectability

There are two possible reasons why $^{129}I$ cannot be detected: (1) the amount of $^{129}I$ is small or (2) a large amount of $^{127}I$ causes interference. Detection or nondetection should not be judged solely based on the lower detection limit of the $^{129}I$ radioactivity concentration. When the amount of $^{127}I$ is so large that the $IH^2$ (ID) correction cannot be applied, it is appropriate to judge the result as nondetection. For samples in which $^{129}I$ is detected before correction but the isotopic ratio of the sample is less than the correction applicability criterion, measurement by AMS is recommended.

[*253] The mass discrimination effect is a phenomenon in which the transmission efficiency of elemental ions differs depending on the mass of the element. A method of correcting the mass discrimination effect is to use a solution with a known isotopic ratio.

Figure II.3.3 shows an example of a flowchart for determining detectability.

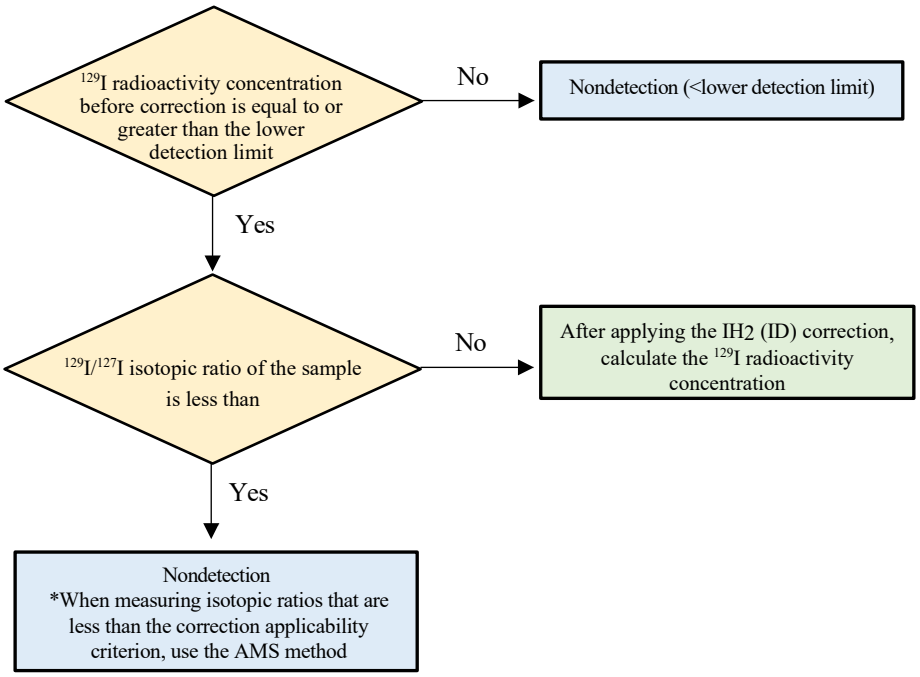



Figure II.3.3 Flowchart for the determination of detectability

### 3.5.3 Uncertainty

The uncertainty of measurement is used as an indicator of how reliable a measurement result is. The uncertainty of measurement is defined as "a parameter, associated with a measurement result, that characterizes the dispersion of values that could reasonably be attributed to the quantity being measured"[*254]. It is important to note that the uncertainty of measurement does not represent the variability of individual measurement results.

Rather, it represents the potential variability inherent in a series of measurements.

In conventional ICP–MS analysis, it is a common practice to determine and report only the uncertainty from repeated measurements (standard deviation). Although counting uncertainty is dominant in the analysis of low-level environmental samples, there exist additional sources of uncertainty throughout the analytical process, including sample pretreatment and instrument calibration. By evaluating uncertainty, it becomes possible to judge agreement or disagreement among analytical results from different laboratories in proficiency testing and interlaboratory comparisons. Furthermore, by identifying the steps that contribute the most to uncertainty and implementing measures to reduce their uncertainties, it is possible to improve the quality of analytical results.

### 3.5.4 Lower Detection Limit

The lower detection limit in the measurement of radionuclides by mass spectrometry varies depending on factors such as the amount of sample used for analysis, dilution factor, and blank counting rate. Therefore, an appropriate lower detection limit should be established according to the purpose of the analysis and measurement. Calculating the lower detection limit provides an indicator of the minimum analyte concentration that can be reliably detected by the measurement. Because environmental radionuclides are often present at trace levels and are frequently not detected, it is desirable to determine the lower detection limit when measuring analytical samples. It should be noted that concentrations higher than the lower detection limit will be detected in most cases. However, concentrations below the lower detection limit do not necessarily result in nondetection. There remains a possibility that they may be detected.

Methods for calculating the lower detection limit include Kaiser's method[*255,*256] and evaluation methods specified in JIS K 0133[*257]. For each lower detection limit concept, it is necessary to consider the distribution of measurement values. When measurements of a given analyte are repeated a sufficient number of times, the resulting values can be described by a normal (Gaussian) distribution, with the mean value located at the peak of the distribution, as illustrated in Figure II.3.4.

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

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

[*256] 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 and Apply Chemistry, 45, 105-123 (1976)

[*257] JIS K 0133: 誘導結合プラズマ質量分析通則 (2022)

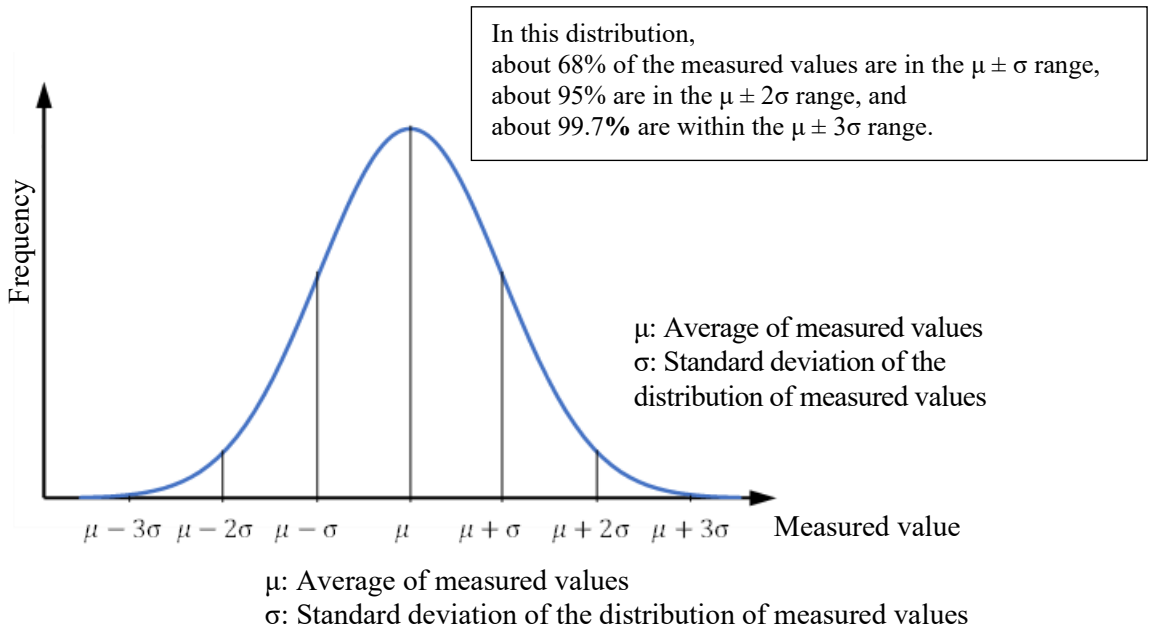



Figure II.3.4. Distribution of measured values

According to JIS K 0133, there are two types of lower detection limits for ICP–MS: the instrument detection limit and the method detection limit. The instrument detection limit, calculated from the standard deviation of the calibration blank solution, is primarily used to monitor instrument performance. The method detection limit, which is calculated from the standard deviation of the procedural blank, is mainly used for routine analyses and for evaluating newly developed analytical methods.

Although there are multiple methods and types for evaluating lower detection limits, the selection should be based on the requirements and specifications of the survey in which the measurement is conducted. When reporting a lower detection limit, it is necessary to clearly state the evaluation method employed.

# Chapter 4 Quality Assurance

In addition to performing analysis and measurements in accordance with the procedures described in this document, it is extremely important to ensure traceability to national standards and to conduct routine inspections to ensure the integrity of instruments. By continuously implementing these practices, it is possible to demonstrate to third parties that the quality of the analytical results is assured. To ensure the quality of analytical results, it is recommended to follow the principles of ISO/IEC 17025. Quality assurance can be broadly divided into internal quality control conducted by the analysts themselves and external quality control, such as through participation in proficiency testing conducted by external organizations.

## 4.1 Internal Quality Control

### 4.1.1 Ensuring Traceability

In $^{129}I$ analysis results, the items for which traceability should be ensured include radioactivity (Bq) and mass (kg). For the former, traceability must be ensured for the triple quadrupole ICP–MS device calibrated using standard solutions. For the latter, traceability must be ensured for electronic balances used during preparation of analytical samples. When analysts prepare calibration standard solutions themselves, they can obtain standard solutions that are traceable to national standards, accompanied by calibration certificates issued by calibration service providers registered under the Measurement Act. For electronic balances, calibration services provided by the manufacturer can be used. Maintenance and inspection, including issuance of calibration certificates, should be performed. Instrument calibration should be performed at appropriate intervals. Further, it is necessary to manage calibration validity periods by setting expiration dates. Within the validity period, it should be confirmed, as described in “4.1.2 Routine Inspection,” that no changes affecting analytical results have occurred in the instruments.

In the same manner, traceability must be ensured for records accompanying analytical results. Specifically, it is important that sampling records documenting the sampling date and location, unique identifiers (analysis numbers, etc.) used to identify analysis samples, and various records and forms generated during analytical and measurement operations are managed in a continuously linked and traceable manner.

### 4.1.2 Routine Inspection

The inspection items and methods for instruments used in $^{129}I$ analysis and measurement are described below. To determine whether instruments are in the proper condition and suitable for use, it is necessary to establish acceptance criteria for each inspection item. It is recommended to establish provisional criteria based on experimentally obtained initial data and then re-establish the acceptance criteria[*258] via statistical processing once data has been accumulated. It is sufficient to confirm that no changes affecting the analysis results have occurred in the instrument; hence, a method different from the one described here may be used. The routine inspection date, person in charge, and inspection results should be recorded.

If the results of the routine inspection do not meet the acceptance criteria, use of the instrument should be temporarily suspended and the cause should be investigated and resolved. If the cause cannot be resolved by re-measurement or reconfiguration of the instrument by the user, inspection or repair by the manufacturer should be performed.

(1) Triple quadrupole ICP–MS

Periodically inspect the triple quadrupole ICP–MS device to ensure that no changes have occurred in the instrument that would affect the analytical results[*259]. It is recommended to conduct this inspection each time measurements are performed.

1) Checks during instrument start-up

- Refer to "3.2.2 Premeasurement Checks" through "3.2.4 Instrument Adjustment" in "Chapter 3 Measurement."

2) Checks during instrument adjustment

- Sensitivity
- Instrument background
- Oxide ion and divalent ion formation ratios
- Short-term stability
- Mass resolution

3) Confirmation of the calibration curve

- Linearity of the calibration curve

(2) Electronic balance

Inspect the electronic balance periodically to ensure that no changes have occurred in the instrument that would affect the analysis results. It is recommended to conduct preuse inspection each time the balance is used as well as periodic inspections on a monthly basis or at similar intervals.

[*258] It is convenient to determine the mean and standard deviation and use the range of $\pm k\sigma$ (k = 2 or 3) centered on the mean as the acceptance criterion.

[*259] For details, refer to "JIS K 0133: 誘導結合プラズマ質量分析通則 (2022)."

- Preuse inspection

  This inspection is performed before using the balance. For balances equipped with an internal calibration weight, it is advisable to perform internal calibration in advance. Using a calibration weight close to the mass of the actual sample (or to the lower limit of the usable range)[*260], perform the preuse inspection of the electronic balance, and confirm that the weighing result is within the acceptance criteria[*261]. Performing the same inspection after using the balance is also recommended.

- Periodic inspection

  Using a calibration weight with a mass close to the maximum weighing capacity of the electronic balance, verify the sensitivity of the balance. For balances equipped with an internal calibration weight, it is advisable to perform internal calibration in advance. The grade of the calibration weight and the acceptance criteria may follow those used for the preuse inspection. This inspection should be performed at fixed intervals. It is recommended to perform it approximately once per month.

(3) Micropipettes

Inspect the micropipettes periodically to ensure that no changes have occurred that would affect the analysis results. It is recommended to conduct preuse inspection each time the micropipettes are used.

- Preuse inspection

Using the micropipette, dispense 1 mL of ultrapure water and weigh it with an electronic balance. Adjust the micropipette so that the measured mass is 1 g. Confirm that the weighing result falls within the acceptance criteria specified in the calibration certificate for the micropipette.

For micropipettes, periodic inspections should also be conducted once a year by the manufacturer or other qualified organization.

(4) Management of reagents and reference materials

Reagents and reference materials that have a guaranteed shelf life should be used within that period. For those without a specified shelf life, quality control should be ensured by managing information such as the date of opening and other relevant records.

## 4.2 External Quality Control

### 4.2.1 Interlaboratory Comparison

The validity of the measurement and data analysis processes should be verified by conducting

[*260] Calibration weights with a calibration certificate (OIML (JIS) Class F2 or higher) are desirable.

[*261] Although the acceptance criteria should be determined based on weighing uncertainty, the minimum weighing value, and a safety factor, an initial control range of 0.5% may be adopted (e.g., when using a 10-g calibration weight, the acceptance criteria would be 9.95–10.05 g.)

interlaboratory comparative analyses using identical samples—preferably with laboratories accredited to ISO/IEC 17025—and confirming that no statistically significant differences are observed among the analytical results.

### 4.2.2 Proficiency Test

By participating in proficiency testing programs conducted by external organizations (preferably organizations accredited to ISO/IEC 17043) and comparing the analytical results of test items with the assigned (reference) values, a laboratory can objectively demonstrate its competence. In proficiency testing conducted in accordance with ISO/IEC 17043, performance evaluation metrics such as Z-scores and En-scores are used to evaluate the performance of participating laboratories.

# Explanation

# Explanation A Interference Factors in Triple Quadrupole ICP–MS

The principal sources of interference in ICP–MS include spectral interferences, nonspectral interferences, and peak tailing, in which the tail of an adjacent isotope peak contributes signal at *m/z* values of ±1. In single-quadrupole instruments, where abundance sensitivity was on the order of $10^{-6}$–$10^{-7}$, tailing was a major factor that interfered with measurements. However, the abundance sensitivity in triple quadrupole ICP–MS has improved to $10^{-11}$ or less. Because the interference from hydrides of $^{127}I$ (at the level of $10^{-8}$–$10^{-9}$) at *m/z* 129 is far greater than the contribution from the tailing of $^{127}I$, the effect of tailing can be ignored.

## A.1 Spectral Interference

In ICP–MS, spectral interference, wherein signals from isobaric species or polyatomic ions overlap with that of the measured isotope, is a significant issue. In the analysis of $^{129}I$ using triple quadrupole ICP–MS, the principal sources of spectral interferences are the dihydride of stable iodine $^{127}I$, $^{127}I^1H_2$, or its deuterated form, $^{127}I^2D$; oxide ions of molybdenum and cadmium ($^{97}Mo^{16}O_2$ and $^{113}Cd^{16}O$); and $^{129}Xe$ present in the argon gas.

### A.1.1 $^{127}I$ Hydrides

(1) Measures against $^{127}I$ hydrides

Interference from $^{127}I^1H_2$ ($^{127}I^2D$) becomes significant in seaweed samples where the $^{127}I/^{129}I$ isotopic ratio is lower than the instrument's $IH_2$ (ID) formation ratio and the concentration of $^{127}I$ is high.

To avoid mistaking the counting rate of $^{127}I^1H_2$ ($^{127}I^2D$) for that of $^{129}I$, the following two measures can be undertake:

① Adjust the sample amount for analysis and/or the dilution factor to reduce the formation of $^{127}I^1H_2$ ($^{127}I^2D$);

② Calculate the amount of $^{127}I^1H_2$ ($^{127}I^2D$) formed and subtract it from the measured value[*262].

In measure ①, the amount of $^{127}I$ in the measured sample is reduced by using a smaller sample mass and a higher dilution factor, decreasing the formation of $^{127}I^1H_2$ ($^{127}I^2D$) from $^{127}I$. The principle is as follows: if the counting rate of $^{127}I^1H_2$ ($^{127}I^2D$) is reduced to the background level, its contribution to the signal at *m/z* 129 becomes negligible. Table II.A.1 shows calculated values of $^{127}I^1H_2$ ($^{127}I^2D$) for different combinations of analytical sample amount and dilution factor for seaweed samples. Although this approach is straightforward, reducing the sample amount and increasing the dilution factor result in an increased lower detection limit; therefore, this method is difficult to apply when a specified low detection limit is required. Further, as the lower detection limit increases, the minimum detectable $^{129}I/^{127}I$ isotopic ratio increases; hence, care must be taken to ensure that the target value is not exceeded. For the purpose of this document, measure ② was adopted because it leads to a smaller lower detection limit and isotopic ratio.

[*262] Refer to "3.5.1 Calculation of $^{129}I$ Radioactivity Concentration" in "Chapter 3 Measurement."

Table II.A.1 Calculated values of $^{127}I^{1}H_2$ ($^{127}I^{2}D$) and detectable levels in seaweed samples

| Sample amount used for analysis (g; dry) | Dilution factor | Calculated $^{127}I^{1}H_2$ ($^{127}I^{2}D$) value (cps)※1,※2 | Detectable level (Bq/kg raw)※2,※3 | Detectable $^{129}I/^{127}I$ isotopic ratio※4,※5 | Target lower detection limit [Isotopic ratio※4] (Bq/kg raw)※6 |
|---|---|---|---|---|---|
| 0.1 | 500 | 0.01 | 3 | $3 \times 10^{-7}$ | 0.1 [$1 \times 10^{-8}$] |
| | 100 | 0.03 | 0.5 | $6 \times 10^{-8}$ | |
| | 10 | 0.26 | 0.05 | $(6 \times 10^{-9})$ | |
| 0.6 | 2500 | 0.01 | 2 | $3 \times 10^{-7}$ | |
| | 100 | 0.16 | 0.09 | $1 \times 10^{-8}$ | |
| | 10 | 1.56 | 0.01 | $(1 \times 10^{-9})$ | |
| 2 | 5000 | 0.01 | 1 | $2 \times 10^{-7}$ | |
| | 100 | 0.52 | 0.03 | $(3 \times 10^{-9})$ | |
| | 10 | 5.20 | 0.003 | $(3 \times 10^{-10})$ | |

※1 The $IH_2$ (ID) formation ratio was $8 \times 10^{-9}$, collection solution mass was 20 g, and sensitivity was 10 cps per 1 ng/L of $^{129}I$.

※2 The $^{127}I$ concentration in seaweed was set to 1300 mg/kg (raw), and the dry weight to raw sample weight ratio was set to 20%.

※3 The lower detection limit for the method was set to 0.02 ng/L, and the specific activity was set to $6.53 \times 10^{6}$ Bq/g.

※4 The $^{129}I/^{127}I$ isotopic ratio was calculated by dividing the detectable level of $^{129}I$ or the target lower detection limit by the $^{127}I$ concentration in seaweed.

※5 Isotopic ratios that do not meet the correction applicability criterion ($9 \times 10^{-9}$) in this measurement method are shown in parentheses.

※6 This is the lower detection limit set as a target in various surveys under the Comprehensive Radiation Monitoring Plan.

(2) Dihydride formation ratio

To determine the appropriate $^{127}I$ concentration and measurement frequency for calculating the $IH_2$ (ID) formation ratio required to evaluate $^{127}I^{1}H_2$ ($^{127}I^{2}D$) formation, the effects of $^{127}I$ concentration, measurement repeatability, and day-to-day variation on the $IH_2$ (ID) formation ratio should be investigated.

1) Effect of $^{127}I$ concentration

① Procedure

Samples with the following $^{127}I$ concentrations were prepared, and measurements and calculation of the $IH_2$ (ID) formation ratio were performed according to the procedure described in "3.4 Confirmation of the Dihydride Formation Ratio" in "Chapter 3 Measurement."

• $^{127}I$ concentrations: 50, 200, 400, 500, and 800 mgI/L (0.5% TMAH solution)

• Measurement parameters: $^{129}I$ measurement conditions (refer to "Explanation C

Example of Measurement Parameters" for more details)

② Results

The correlation plot between the net counting rate at *m/z* 129 and 127 as well as the $IH_2$ (ID) formation ratios at different $^{127}I$ concentrations are shown in Figure II.A.1. The linearity was generally good. Regarding the $IH_2$ (ID) formation ratio, the result at 50 mgI/L largely deviated from those at the other concentrations.

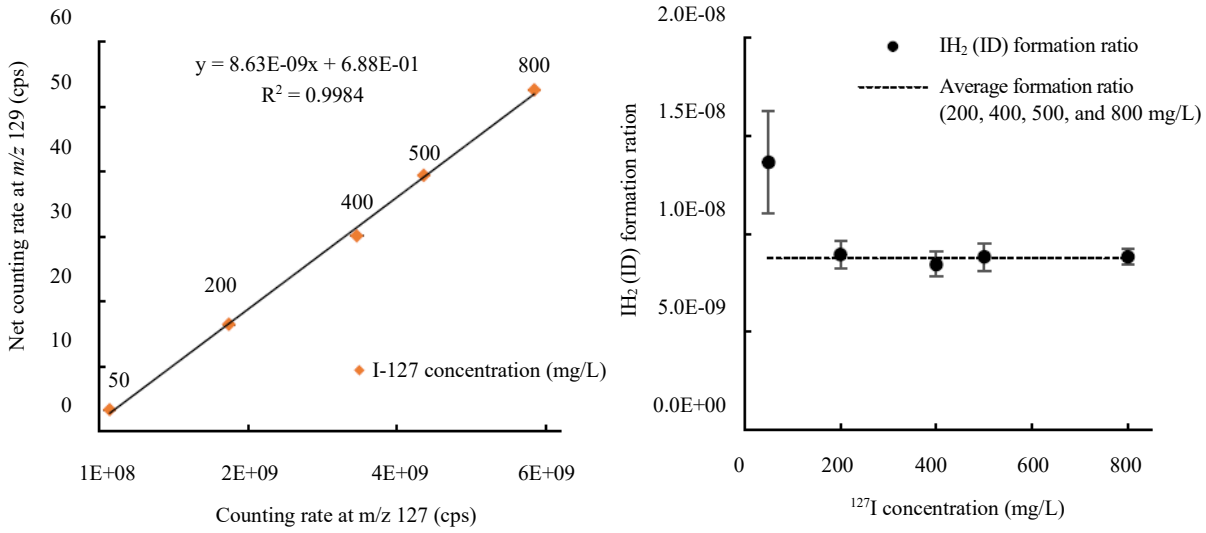



Figure II.A.1 (Left) Correlation between the counting rates at *m/z* 127 and 129. (Right) $IH_2$ (ID) formation ratio as a function of the $^{127}I$ concentration

2) Repeatability

① Procedure

Samples containing $^{127}I$ at concentrations listed below were prepared. The oxygen flow rate was varied, and measurements and calculation of the $IH_2$ (ID) formation ratio were performed according to the procedure described in "3.4 Confirmation of the Dihydride Formation Ratio" in "Chapter 3 Measurement." Repeated measurements were performed on the same sample under the following conditions:

- Measurement sample : 400 mgI/L (0.5% TMAH solution)
- Oxygen flow rate : 1.05 mL/min or 1.2 mL/min
- Repeatability : Measured three times on the same day (a blank was measured between samples)
- Daily variation : Measured over 3 days

② Results

The results of the repeatability inspection are shown in Figure II.A.2. The repeatability was stable for both flow rates; however, daily variation showed noticeable variability.

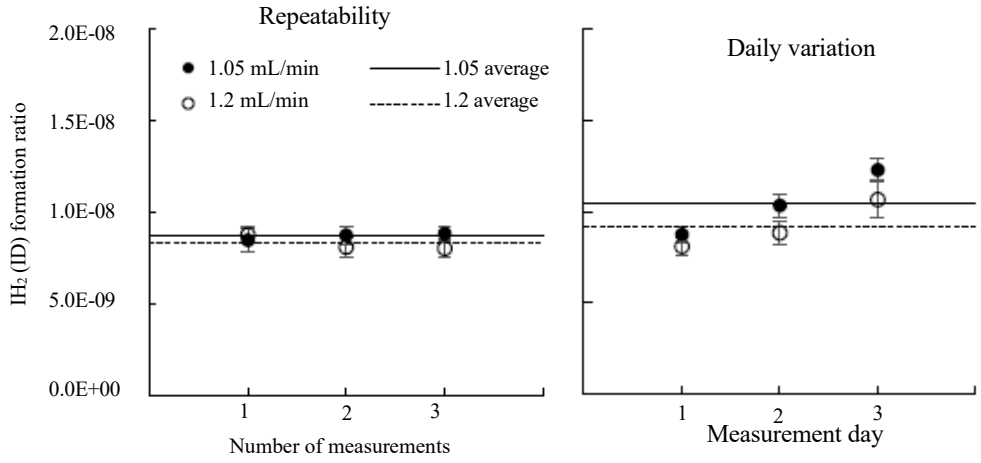



Figure II.A.2 Repeatability and daily variation of the $IH_2$ (ID) formation ratio

3) Summary

Because the $IH_2$ (ID) formation ratio showed less variability at higher $^{127}I$ concentrations, a concentration of 400 mgI/L was used for the purpose of this document. Since daily variations were observed, it is desirable to perform measurements on a regular basis.

Here, the $IH_2$ (ID) formation ratio was approximately $8 \times 10^{-9}$. Meanwhile, Ohno et al. reported a value of $5 \times 10^{-9}$ in a report[*263]. Although the present results indicate that increasing the oxygen flow rate can reduce the $IH_2$ (ID) formation ratio, this may also lead to an increase in the lower detection limit due to decreased sensitivity. Therefore, it is necessary to determine an appropriate flow rate in advance (refer to "Explanation C Example of Measurement Parameters" for details).

## A.1.2 Molybdenum and Cadmium

Molybdenum and cadmium are present in environmental samples and have high oxide formation ratios. Their oxide species, $^{97}Mo^{16}O_2$ and $^{113}Cd^{16}$, respectively, may interfere during $^{129}I$ measurement. The presence or absence of these interferences should be confirmed by measuring the molybdenum and cadmium counting rates for each sample. The criteria for determining no impact and the allowable upper limit of the counting rate should be examined in advance. If the allowable upper limit of the counting rate is exceeded, implement measures such as increasing the dilution factor of the measurement sample.

An example of how to examine the allowable upper limit of the counting rate is provided below.

(1) Dilute a molybdenum standard solution or a cadmium standard solution to prepare calibration standards with concentrations of 0, 100, 500, and 1,000 μg/L (0.5% TMAH solution) separately for both elements.

[*263] T. Ohno et al.: Determination of ultratrace 129I in soil samples by Triple Quadrupole ICP-MS and its application to Fukushima soil samples, Journal of Analytical Atomic Spectrometry, 28, 1283-1287 (2013)

(2) Measure each standard solution using triple quadrupole ICP–MS under the following conditions.

・Conditions : $^{129}$I measurement conditions (refer to "Explanation C Example of Measurement Parameters")

・Measured masses : Molybdenum: *m/z* 97 → 129 and *m/z* 129

Cadmium: *m/z* 111 and *m/z* 129

(3) Subtract the counting rate of the calibration blank from the *m/z* 129 counting rate to obtain the net *m/z* 129 signal, and plot a graph with the net m/z 129 counting rate on the vertical axis.

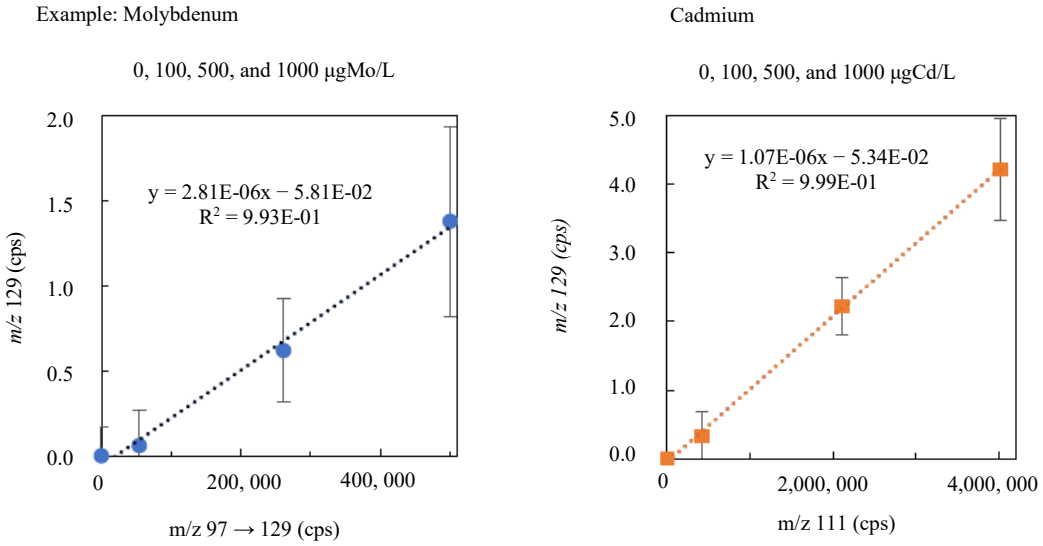



Figure II.A.3 Changes in the signal at *m/z* 129 as a function of the counting rates of molybdenum (left) and cadmium (right).

(4) Determine the maximum allowable interference at *m/z* 129, expressed in cps. Here, the counting rate of 0.05 cps detected at *m/z* 129[*264] is the allowable upper limit of the counting rate for molybdenum or cadmium.

(5) Calculate the allowable upper limit of the counting rate for molybdenum or cadmium from the slope of the calibration curve[*265]. To ensure a conservative evaluation, the intercept is not taken into account.

Example: Allowable upper limit of the counting rate for molybdenum

$$m/z\ 97 \rightarrow 129\ (\text{cps}) = 0.05/(2.81 \times 10^{-6}) = 17{,}800\ (36\ \mu\text{gMo/L})$$

[*264] The allowable value was set as one-tenth of the background counting rate, assuming a background counting rate of 0.5 cps.

[*265] Ohno et al. reported that in measurements of soil samples using an Agilent 8800 triple quadrupole ICP–MS device, molybdenum and cadmium concentrations that caused 0.2 cps interference at m/z 129 were 20 ppb and 10 ppb, respectively (T. Ohno et al.: Determination of ultratrace $^{129}$I in soil samples by Triple Quadrupole ICP-MS and its application to Fukushima soil samples, Journal of Analytical Atomic Spectrometry, 28, 1283-1287 (2013)). The allowable values obtained in the present example differ from those reported in the cited paper, indicating that evaluation must be carried out for each instrument.

Allowable upper limit of the counting rate for cadmium

$m/z$ 111 → 129 (cps) = 0.05/(1.07 × $10^{-6}$) = 46,700 (12 $\mu$gCd/L)

### A.1.3 $^{129}$Xe in Argon Gas

Argon gas used for plasma generation contains trace amounts of xenon, and it is known that $^{129}$Xe interferes at *m/z* 129. During $^{129}$I measurements, $^{129}$Xe is removed by introducing oxygen gas. Figure II.A.4 shows the results obtained when *m/z* 129 was measured with an oxygen flow rate of 0 mL/min.

At *m/z* 129, interference on the order of several thousand counts per second was observed. Therefore, removal of $^{129}$Xe by oxygen is essential when performing measurements aimed at reducing the lower detection limit.

Measurement conditions: $^{129}$I measurement conditions (refer to "Explanation C Example of Measurement Parameters," with an oxygen flow rate of 0 mL/min)

Repeated measurements: 1 measurement × 4 days

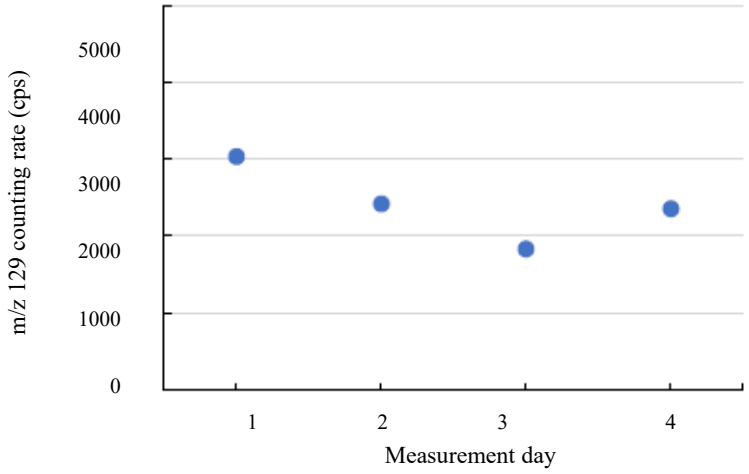



Figure II.A.4 Counting rate at *m/z* 129 with an oxygen flow rate of 0 mL/min

## A.2 Nonspectral Interferences

### A.2.1 Physical Interference

Variations in the concentrations of acids or bases and coexisting components in the measurement sample cause variations in the atomization efficiency of the nebulizer, which causes fluctuations in the counting rate. This physical interference can be reduced by matching the liquid properties of the calibration standard and the measurement sample using internal-standard correction or other methods.

High salt concentrations cause salts to precipitate on the sampling cone and skimmer cone, reducing the orifice diameter and leading to a decrease in sensitivity. Under normal plasma conditions, it is desirable to keep the salt concentration within 0.1%.

### A.2.2 Ionization Interference

When large amounts of elements with low ionization energies, such as alkali metals or alkaline earth metals, are present, the ionization efficiency of the analyte element can change significantly. This type of interference can sometimes be reduced by internal-standard correction.

### A.2.3 Matrix Interference

A phenomenon wherein the presence of a large number of coexisting elements generally decreases the counting rate of the analyte element. This type of interference can be reduced by internal-standard correction.

### A.3 Examination of the Effects of Salts

The measurement samples analyzed using the iodine determination method consist primarily of sodium chloride in seawater samples and sodium sulfite in seaweed samples. The total salt concentration of seawater is generally ~3.4%, of which sodium chloride accounts for 2.7%. Therefore, the sodium chloride concentration in a seawater sample diluted 50-fold is estimated to be 0.05%. The iodine collection solution for seaweed samples contains a sodium sulfite concentration of 0.5%, which becomes 0.01% after 50-fold dilution. The potential effects of these salts on $^{129}I$ measurement were examined. Since the $^{129}I$ standard is valuable, $^{127}I$ was used for this examination. To investigate the effects of salts, the signal at *m/z* 127 was monitored as an indicator of iodine sensitivity, while the signal at *m/z* 129 was monitored as background.

#### A.3.1 Verification Procedure

Solutions containing sodium chloride or sodium sulfite were prepared in 0.5% TMAH, with $^{127}I$ at a concentration of 10 µgI/L and salt concentrations of 0, 0.01, 0.05, 0.1, and 0.3%. The measurements were performed three times for 3 days under the following conditions.

- Measurement conditions : $^{127}I$ measurement conditions (refer to "Explanation C Example of Measurement Parameters")
- Integration time : 1 sec for *m/z* 127 and 10 sec for *m/z* 129
- Repeated measurements : 3 measurements × 3 days

#### A.3.2 Sodium Chloride

Figure II.A.5 shows the 3-day average counting rates and the sodium chloride concentrations. The $^{127}I$ counting rate reached its maximum at a concentration of 0.01% and decreased as the concentration increased further. This is considered to be due to physical interference or matrix effects.

The background counting rate at *m/z* 129 showed a slight increase at 0.01%, remained nearly constant up to 0.1%, and increased at 0.3%. Although the cause is unclear, these results indicate that samples with high sodium chloride concentrations may cause interference at *m/z* 129.

It is therefore concluded that keeping the sodium chloride concentration at 0.1% or lower will not significantly affect $^{129}I$ measurements. For seawater samples with a sodium chloride concentration of 3%, 50-fold dilution results in a concentration of ~0.06%.

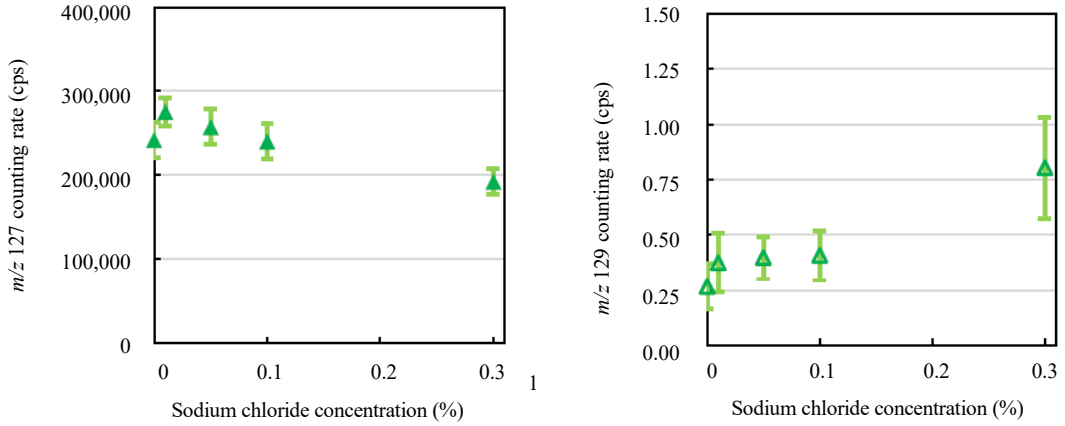


Figure II.A.5 Changes in the counting rates at *m/z* 127 (left) and *m/z* 129 (right) as a function of the sodium chloride concentration

### A.3.3 Sodium Sulfite

Figure II.A.6 shows the 3-day average counting rates and the sodium sulfite concentrations. The $^{127}I$ counting rate increased at 0.01% and then remained nearly constant. This result was due to physical interference or matrix effects. Notably, the effect was found to be weaker than that of sodium chloride.

The background counting rate at *m/z* 129 increased with increasing concentration. At 0.3%, it increased markedly to nearly six times that observed at 0%.

For seaweed samples, it is desirable to dilute the sample so that the sodium sulfite concentration is ≤0.1%. After 50-fold dilution, the sodium sulfite concentration in the iodine collection solution decreases from 0.5% to 0.01%.

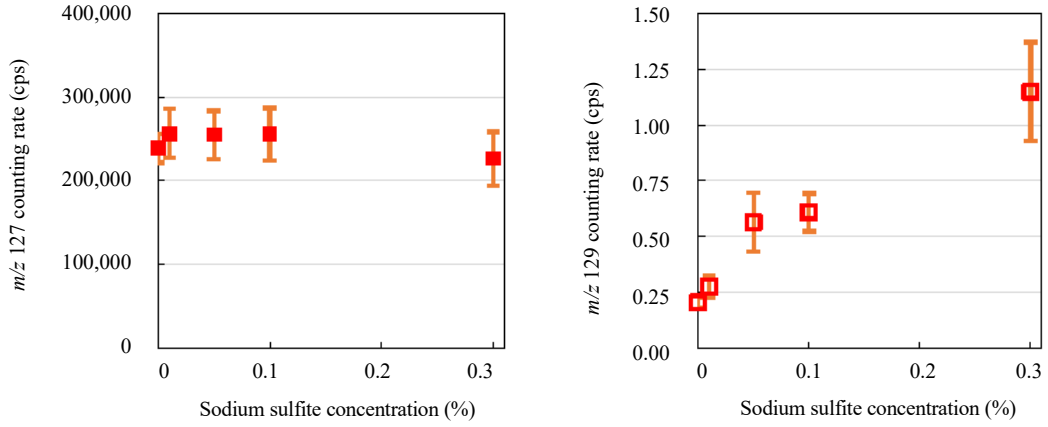



Figure II.A.6 Changes in the counting rates at *m/z* 127 (left) and *m/z* 129 (right) as a function of the sodium sulfite concentration

### A.3.4 Summary

The results indicate that an increase in the salt concentration may lead to an increase in the background signal at *m/z* 129. Although the cause of this background increase is unclear, possible explanations include the influence of trace components in reagents or the washout of residual $^{129}I$ in the instrument. Because similar results were obtained over 3 days of measurements, a certain degree of reproducibility can be assumed. However, since this phenomenon occurs at extremely low counting rates on the order of ~1 cps, careful judgment is required.

Based on the results of this study, it is considered that the effects of the sodium chloride concentration in seawater samples and the sodium sulfite concentration in seaweed samples is minimal on $^{129}I$ measurements if the concentrations are kept at ≤0.1%. These salt concentrations are the same as those generally recommended for ICP–MS analyses. Under normal analytical conditions, the effect of salts can be regarded as negligible.

# Explanation B Determination of $^{127}I$

Given the limited availability of reference materials with certified or reference values for detectable $^{129}I$ concentrations applicable to this method, validation of the analytical process should be performed through the determination of $^{127}I$.

The procedure for the determination of $^{127}I$ is described below.

## B.1 Preparation of Measurement Samples

### B.1.1 Seawater

Prepare samples in the same manner as described in "Chapter 1 Seawater."

### B.1.2 Seaweed

Prepare samples in the same manner as described in "Chapter 2 Seaweed." Because seaweed samples prepared for $^{129}I$ measurement have low dilution factors and extremely high $^{127}I$ concentrations, it is preferable to prepare $^{127}I$ measurement samples separately from $^{129}I$ measurement samples.

The $^{127}I$ concentration in seaweed varies greatly depending on the species. The dilution factor for $^{127}I$ measurement samples should be adjusted according to the $^{127}I$ concentration in the sample so that the concentration falls within the calibration range. Here, an example is provided assuming a $^{127}I$ concentration of 500 mg/kg (raw) in seaweed and a dilution factor of 25,000.

(1) Instruments and reagents

Those required for preparing measurement samples as described in "2.1 Equipment, Instruments, and Reagents" in "Chapter 2 Seaweed."

(2) Operation

Prepare samples as follows after analysis according to "2.2.2 Iodine Capture by Thermal Hydrolysis" in "2.2 Thermal hydrolysis" of "Chapter 2 Seaweed Samples."

1) Using a micropipette, take 1 g of the collection solution prepared as per "2.2.2 Iodine Capture by Thermal Hydrolysis" and transfer it to a 50 mL volumetric flask.
2) Add 1 mL of the 25% TMAH solution.
3) Add ultrapure water up to the calibration mark of the volumetric flask and mix thoroughly by shaking.
4) Pour the solution in the volumetric flask into a beaker and take 0.1 mL using a micropipette.
5) Transfer it to a 50 mL volumetric flask.
6) Add 1 mL of the 25% TMAH solution to this volumetric flask.
7) Add ultrapure water up to the calibration mark of the volumetric flask.
8) Mix thoroughly and use it as the sample for $^{127}I$ measurement.

## B.2 Preparation of Solutions for Generating the Calibration Curve

Dilute a $^{127}I$ solution prepared from potassium iodide to prepare a calibration solution. Commercially available standard solutions may also be used. Before analysis, it is necessary to confirm whether a standard solution with a certified $^{127}I$ concentration value can be used.

(1) Instruments

Use the instruments described in "3.1.1 Equipment, Instruments, and Reagents" mentioned in "3.1 Preparation of Calibration Solutions" of "Chapter 3 Measurement."

(2) Reagents

1) $^{127}I$ solution (100 $\mu$gI/L; prepare as per Section 3.2.1)
2) TMAH solution[*266,*267,*268] (mass fraction 25%)
3) Ultrapure water (purified to a resistivity of 18 MΩ·cm or higher[*269])

(3) Operation

1) Add 0.1, 0.5, 1, 5, and 10 mL of the $^{127}I$ solution (100 $\mu$gI/L) in separate 100 mL volumetric flasks.
2) Add 2 mL of the 25% TMAH solution.
3) Add ultrapure water up to the calibration mark of the volumetric flasks.
4) Mix thoroughly by shaking to obtain $^{127}I$ calibration solutions (0.1, 0.5, 1, 5, and 10 $\mu$gI/L)[*270].

## B.3 Determination of $^{127}I$

Because iodine exhibits a pronounced memory effect, careful consideration should be given to the order of measurements. If the approximate concentrations of the samples are known, it is advisable to conduct measurements starting from the lowest concentration.

[*266] 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 about handling these substances.

[*267] 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." Further, necessary measures must be undertaken to prevent theft, loss, leakage, and other incidents.

[*268] Classified as a Class IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Following precautions are necessary: Open flames must be strictly avoided. Store and handle the material below its flash point. Ensure separate storage from Category I and Category V Hazardous Substances. Implement measures to avoid static electricity generation. When transferring to smaller containers, avoid filling to full capacity to prevent potential rupture due to thermal expansion.

[*269] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

[*270] Use the 0.5% TMAH solution as the calibration blank solution (0 μg/L).

When quantifying $^{127}$I, $^{127}$I and $^{129}$I should be measured separately because the dilution factors of associated measurement samples are different. Measurements should be performed in the order of $^{127}$I first, followed by $^{129}$I. The $^{129}$I measurement sample has a low dilution factor. Further, a high concentration of $^{127}$I is introduced into the instrument during measurement. Therefore, when $^{127}$I is measured after $^{129}$I, prolonged cleaning of the instrument or of the components of the sample introduction system is required.

An additional method to correct for memory effects is to measure the washing solution or calibration blank before and after each sample and subtract the corresponding memory contribution from the sample's counting rate.

(1) Instruments and reagents

Use the instruments and reagents described in "3.2.1 Equipment, Instruments, and Reagents" in "3.2 Measurement Operation" of "Chapter 3 Measurement."

(2) Operation

① Premeasurement checks and instrument adjustment

1) Perform operations according to "3.2.2 Premeasurement Confirmation" through "3.2.4 Instrument Adjustment" described in "3.2 Measurement Operation" of "Chapter 3 Measurement."

② Preliminary settings

1) Set the *m/z* value to be measured, integration time, number of repetitions, and other conditions[*271]. Measure *m/z* 127 and *m/z* 185
2) Set the rinse time[*272].
3) The autosampler should be programmed with the details of the calibration solutions and measurement samples as well as the measurement order. Assign the positions of the measurement samples in the autosampler, and configure the measurement sequence so that each sample is alternated with a 0.5% TMAH cleaning solution.

③ Determination of $^{127}$I

1) Transfer the calibration solutions and measurement samples into the measurement container.
2) Place the container in the autosampler.
3) Introduce the rhenium internal-standard solution (100 $\mu$g Re/L) via online addition and confirm that the internal-standard signal is stable.
4) Measure the 0.5% TMAH solution as the calibration blank and the calibration solutions, determine the counting rate ratio of *m/z* 127 to 185, and construct a calibration curve relating the $^{127}$I concentration to this counting rate ratio.
5) Add the measurement sample solution, and determine the $^{127}$I concentration ($\mu$g/L) from the counting rate ratio of *m/z* 127 to 185 using the calibration curve.

[*271] Refer to "Explanation C Example of Measurement Parameters" for examples.
[*272] Because iodine shows a strong memory effect, a sufficient rinsing duration is required. It is advisable to determine the required cleaning duration in advance.

## B.4 Calculation of the $^{127}$I Concentration

(1) Net counting rate

Subtract the blank counting rate from the sample *m/z* 127 counting rate to obtain the net counting rate. Because iodine shows a strong memory effect, the average of the premeasurement and postmeasurement counting rates of blanks are subtracted in this measurement method[*273].

$$r_{127n} = r_{127} - (r_{127b1} + r_{127b2})/2$$

$r_{127n}$ : Net counting rate at *m/z* 127 (cps)

$r_{127}$ : Counting rate of the measured sample at *m/z* 127 (cps)

$r_{127b1}$ : Counting rate of the premeasurement blank at *m/z* 127 (cps)

$r_{127b2}$ : Counting rate of the postmeasurement blank at *m/z* 127 (cps)

(2) $^{127}$I concentration in the measurement sample

Based on the gradient, intercept, and internal-standard counting rate of the calibration curve, determine the $^{127}$I concentration in the measured sample as follows:

$$C_s = \frac{\frac{r_{127n}}{r_{is}} - b}{a}$$

$C$s : Concentration of the measurement sample ($\mu$g/L)

$X$is : Counting rate of the internal-standard element (cps)

$a$ : Slope of the calibration curve (cps/(μg/L))

$b$ : Intercept of the calibration curve

(3) $^{127}$I concentration in the sample

The $^{127}$I concentration in the sample is calculated from the dilution factor and the sample volume.

1) Seawater samples

Determine the $^{127}$I concentration in the sample according to the following equation:

$$C_{sp} = \frac{C_s \times V}{W_s}$$

$C$sp : Sample concentration ($\mu$g/L)

$V$ : Volume of the volumetric flask (mL)

$W$s : Sample volume (mL)

[*273] The blank exerting the greatest influence on the measured signal can be identified and selected for subtraction. The types of blanks and the effects they are used to correct are summarized below:

| | |
|---|---|
| Calibration blank | : corrects for background |
| Procedural blank | : corrects for contamination introduced during the analytical process |
| Pre and postmeasurement blanks | : correct for memory effects. |

2) Seaweed samples

Determine the $^{127}$I concentration in the sample according to the following equation:

$$C_{sp} = \frac{C_s \times Z \times w \times D}{W_s \times 100}$$

$C$sp : Sample concentration ($\mu$g/kg raw)

$Z$ : Dry residue (%)

$w$ : Weight of the trapping solution (g)

$D$ : Dilution factor

$W$s : Sample weight (g; dry matter)

## B.5 Verification of the Analytical Procedure

To validate the analytical procedure by quantifying $^{127}$I, reference materials were analyzed. For the CRC gas, measurements were performed not only in the presence of oxygen gas used for $^{129}$I measurements but also under conditions with no gas flow (hereinafter referred to as the "Nogas" condition) and with helium gas flow.

(1) Operation

The reference materials listed in Table II.B.1 were subjected to thermal hydrolysis to prepare measurement samples according to the procedure described in "Chapter 2 Seaweed Samples." $^{127}$I was quantified according to the procedure described in "B.3 Determination of $^{127}$I."

- CRC gas: Nogas, helium gas, or oxygen gas
- Repeated tests: 1 sample × 3 days (NIST SRM 3232 and NIST SRM 1547) 2 samples × 1 day (NIST RM 8435)

Table II.B.1 Standard reference materials

| Reference material | Sample | $^{127}$I concentration (mg/kg dry matter) | Variation (mg/kg dry matter) | Remarks |
|---|---|---|---|---|
| NIST SRM 3232 | Kelp Powder | 944 | 88 (k = 2) | Certified value |
| NIST SRM 1547 | Peach Leaves | 0.3 | -※1 | Reference value |
| NIST RM 8435 | Whole Milk Powder | 2.3 | 0.4 (95% CI) | Reference value |

※1 The standard deviation of results obtained by analysis at the Japan Chemical Analysis Center*274 (number of specimens: 22) was 0.02.

(2) Results

Figure II.B.1 shows the results of $^{127}$I determination when the CRC gas was set to Nogas, helium gas, or oxygen gas. The results are in good agreement and fall within the range of variability of the certified or reference values. For NIST SRM 1547, the indicated range corresponds to three

*274 The analyses were conducted in accordance with "Chapter 4 Seaweed" and "Chapter 7 Measurement" ("7.1 Determination of $^{127}$I by ICP–MS") of "III. AMS."

times the variability of analytical results obtained over the past 10 years at the Japan Chemical Analysis Center.

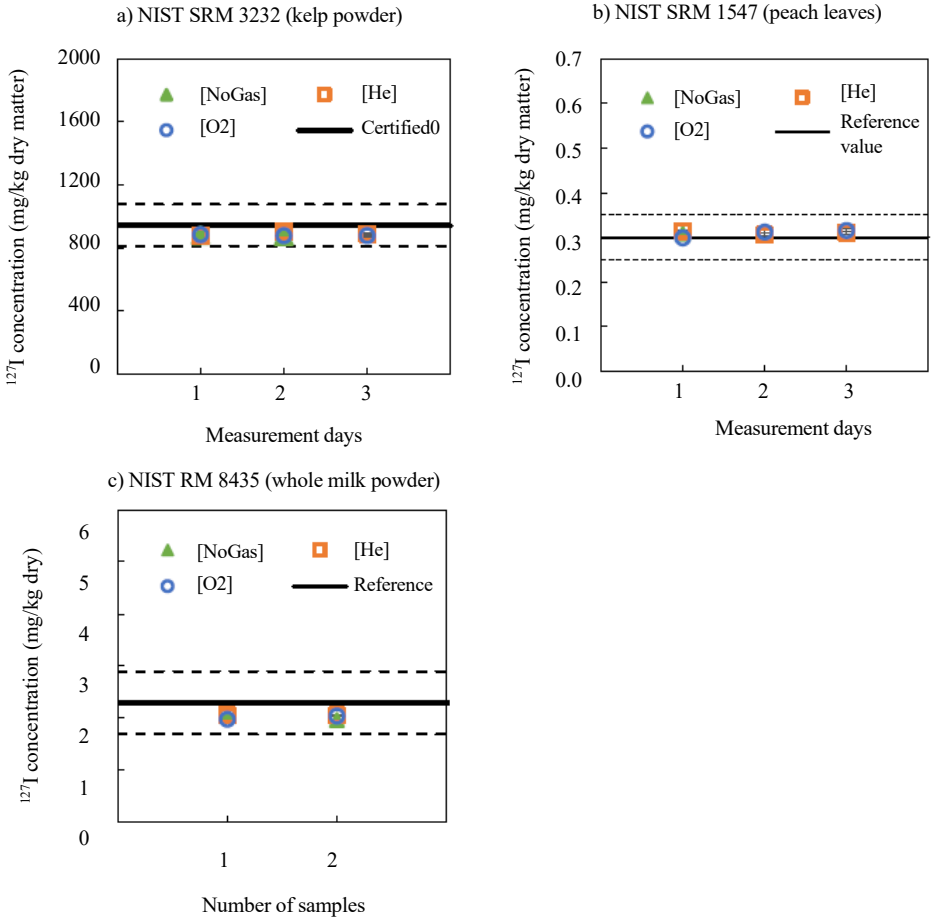



Figure II.B.1 Results of $^{127}$I determination in the standard reference materials

a) Results are obtained by measuring one sample over 3 days. For Nogas, only the results for days 1 and 2 are shown. The indicated range represents the uncertainty (k = 3).
b) Results are obtained by measuring one sample over 3 days. For Nogas, only the results for day 1 are shown. The indicated range represents three times the standard deviation of analytical results obtained at the JCAC (number of samples: 22).
c) Results are obtained by measuring two samples. The indicated range represents the uncertainty (k = 3).

(3) Summary

The $^{127}$I determination results obtained when the CRC gas was Nogas, helium gas, or oxygen gas showed good agreement, confirming the validity of the $^{127}$I analysis process using thermal hydrolysis.

Because certified reference materials for $^{129}$I are limited, verification of the analytical procedure using $^{127}$I reference materials is an effective means of validating the analytical process.

# Explanation C Example of Measurement Parameters

## C.1 Study of the Oxygen Gas Flow Rate

An important goal of optimizing the oxygen gas flow rate in $^{129}$I measurements is to ensure that $^{129}$Xe is sufficiently removed and sufficient sensitivity is achieved. For this purpose, evaluation is commonly performed using the background equivalent concentration (BEC)[*275,*276,*277]. In this measurement method, conditions under which $IH_2$ (ID) correction is effective are defined as those in which the $^{129}I/^{127}I$ isotopic ratio in the sample is equal to or greater than the correction applicability criterion ($IH_2$ (ID) formation ratio + standard deviation). Therefore, it is desirable to set the gas flow rate at which the $IH_2$ (ID) formation ratio is sufficiently low. Direct measurement of the $IH_2$ (ID) formation ratio involves the risk of memory effects due to the use of high concentration $^{127}$I solutions. Accordingly, in this example, evaluation was performed using the IH formation ratio instead.

The *m/z* 127, 128, and 129 counting rates for each oxygen gas flow rate were measured according to "3.3 Optimization of the Oxygen Gas Flow Rate" of "Chapter 3 Measurement." Using the equations provided below, the $^{127}$I sensitivity, IH formation ratio, and BECI$^{129}$ were calculated. The results are shown in Figure II.C.1 (seawater) and Figure II.C.2 (seaweed). The $^{127}$I sensitivity for seawater and seaweed samples reached the maximum at oxygen flow rates of 0.4–0.5 mL/min and decreased as the oxygen flow rate increased beyond this range. The IH formation ratio decreased with increasing oxygen flow rate. *The m/z* 129 counting rate also decreased with increasing oxygen flow rate for the seawater and seaweed samples (indicating the removal of $^{129}$Xe). However, because the $^{127}$I sensitivity simultaneously decreased, the seaweed samples showed a minimum BEC of 1.05 mL/min. For the seawater samples, the BEC was nearly constant from 0.90 mL/min onward, with the minimum value observed at 1.5 mL/min.

In the example, an oxygen gas flow rate of 1.05 mL/min was used because it provided the lowest BEC and favorable IH formation ratio for the seaweed samples. Although the minimum BEC for the seawater samples was observed at 1.5 mL/min, the results at 1.05 mL/min were comparable; therefore, 1.05 mL/min was selected due to higher sensitivity and greater practicality.

(1) Calculation

1) $^{127}$I sensitivity

$$s_{127} = r_{127n}/C_{s127}$$

$s_{127}$ : Sensitivity for $^{127}$I (cps/($\mu$g/L))

$r_{127n}$ : Net counting rate at m/z 127 (cps)

$C_{s127}$ : $^{127}$I concentration in the measurement sample ($\mu$g/L)

[*275] T. Ohno et al.: Determination of ultratrace 129I in soil samples by Triple Quadrupole ICP-MS and its application to Fukushima soil samples, Journal of Analytical Atomic Spectrometry, 28, 1283- 1287 (2013)

[*276] Agilent Technologies: 酸素リアクションモードを用いた7700x ICP-MS による水溶液サンプル中ヨウ素 129 の超微量分析 (5990-8171JAJP) (2013)

[*277] 安積潔 他: ICP 質量分析法による葉菜中のヨウ素-129 分析の検討, 青森県原子力センター所報, 14, 3-17 (2019)

2) IH formation ratio

$$H1 = r_{128n}/r_{127}$$

$H1$ : IH formation ratio

$r_{128n}$ : Net counting rate at *m/z* 128 (cps)

$r_{127}$ : Counting rate at *m/z* 127 (cps)

3) BEC

$$BEC_{129I} = r_{129}/s_{127} \times M_{129}/M_{127} \times 1000$$

$BE_{C129I}$ : BEC of $^{129}$I (ng/L)

$r_{129}$ : Counting rate at *m/z* 129 (cps)

$M_{129}$ : Molar mass of $^{129}$I (g/mol)

$M_{127}$ : Molar mass of $^{127}$I (g/mol)

(2) Measurement conditions

- Measurement conditions : $^{129}$I measurement conditions (refer to "Explanation C Example of Measurement Parameters")
- Integration time : 1 second for *m/z* 127 and 128 and 10 seconds for *m/z* 129

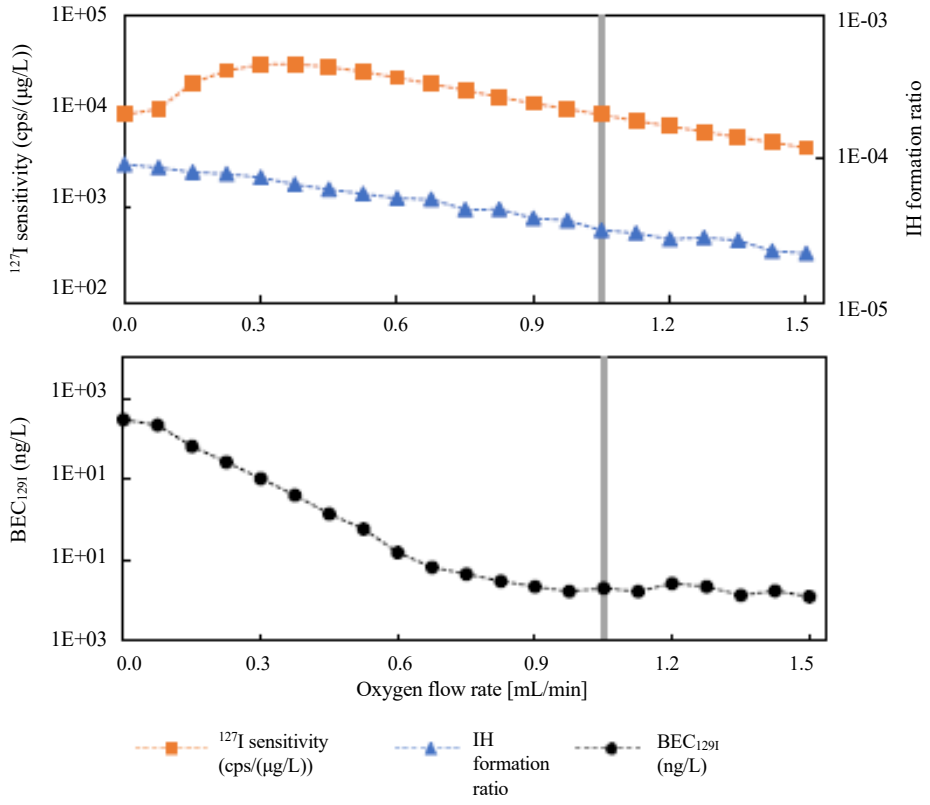



Figure II.C.1 Effect of the oxygen flow rate on $^{127}$I sensitivity, IH formation ratio, and BEC for seawater samples

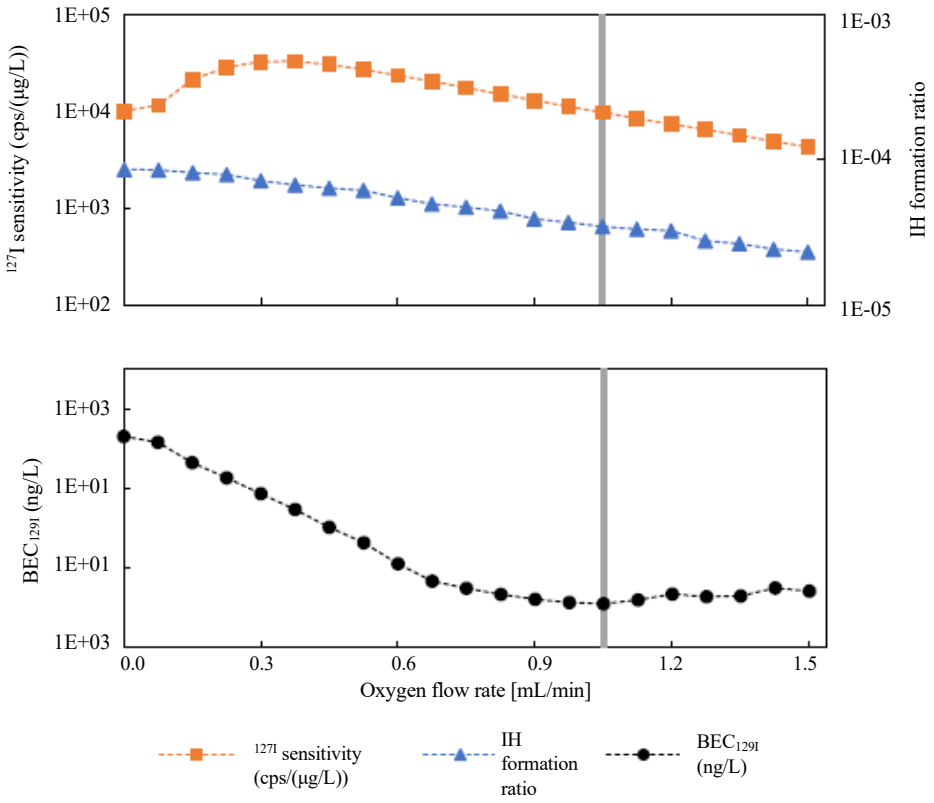



Figure II.C.2 Effect of the oxygen flow rate on $^{127}$I sensitivity, IH formation ratio, and BEC in seaweed samples (sea lettuce)

## C.2 Example of Measurement Parameters

Examples of instrument and measurement parameters of triple quadrupole ICP–MS are presented in Table II.C.1.

Table II.C.1 Examples of parameters in triple quadrupole ICP–MS

| Parameter | $^{129}$I determination | $^{127}$I determination |
|---|---|---|
| Model name | Agilent 8900 | |
| Scan type | MS/MS | |
| RF output | 1550 W | |
| Plasma gas flow rate | 15 L/min | |
| Auxiliary gas flow rate | 1.0 L/min | |
| Nebulizer gas flow rate | 1.0 L/min | |
| Make-up gas flow rate | 0.10 L/min | |
| Spray chamber temperature | 2 °C | |
| Sample flow rate (pump speed) | 300 $\mu$L/min (0.1 rps) | |
| Sampling depth | 8 mm | |
| Potentials of extraction electrodes 1, 2 | 0 V, −200 V | |
| Energy discrimination | −7 V | |
| Number of repetitions | 5 | |
| CRC gas | Oxygen | Oxygen[*278] |
| CRC gas flow rate | 1.05 mL/min | 1.05 mL/min |
| Axial acceleration | 0 V | 1.5 V |
| Integration time | 0.1 sec for *m/z* 97 → 129, 113, and 127<br>1 sec for *m/z* 128 and 185<br>10 sec for *m/z* 129 | 0.1 sec for *m/z* 95 and 111<br>1 sec for *m/z* 127 and 185 |
| Cleaning time (pump speed) | 1) Ultrapure water: 120 sec (0.3 rps)<br>2) 0.5% TMAH solution: 120 sec (0.3 rps) | 1) Ultrapure water: 60 sec (0.3 rps)<br>2) 0.5% TMAH solution: 60 sec (0.3 rps) |

[*278] The CRC gas may be Nogas (no gas flow) or helium gas (refer to "B.5 Verification of the Analytical Procedure" in "Explanation B Determination of $^{127}$I"). An example helium gas flow rate is 3 mL/min.

## C.3. Verification of the Cleaning Time

Due to iodine's strong memory effect, after measuring a sample, sufficient cleaning of the sample introduction pathway is required to avoid affecting the results of subsequent measurements. Therefore, the effectiveness of the cleaning parameters listed in Table II.C.1 in "C.2 Example of Measurement Parameters" was evaluated. At the same time, the cleaning efficiency was evaluated to determine whether it could be improved by extending the cleaning duration and by using a higher-concentration TMAH cleaning solution containing sodium sulfite.

(1) Experimental conditions

The measurement conditions are listed in Table II.C.2, and the solutions used in the study are listed below. For each sample, the introduction time of the cleaning solution was adjusted to be ~30 seconds; thus, repeating measurements for four samples corresponded to a total of ~120 seconds. After measuring the iodine solution, ultrapure water was measured for four samples (~120 seconds), followed by the measurement of the TMAH wash solution for eight samples (~240 seconds). The same experiment was conducted for two types of TMAH cleaning solutions.

- Iodine solution : (1 mgI/L; with the 0.5% TMAH solution)
- Ultrapure water : (purified to a resistivity of 18 MΩ·cm or higher[*279])
- TMAH cleaning solution : (0.5% TMAH solution or 1% TMAH + 0.01% sodium sulfite solution)

Table II.C.2 Measurement conditions for studying the effect of the cleaning time※1

| Parameter | Set time (seconds) | Pump speed (rps) |
|---|---|---|
| Cleaning time | 20 | 0.3 |
| Stabilization time | 10 | 0.3 |
| *m/z* 127 integration time (repetitions) | 1 (3 times) | 0.1 |
| Probe cleaning | 1 | 0.3 |

※1 The cleaning operations actually performed were limited to those listed in this table. All other measurement parameters were the same as those in $^{127}$I measurements (refer to "Table II.C.1" in "C.2 Example of Measurement Parameters").

(2) Results of the verification

The relative intensity of *m/z* 127, when the measured value of the iodine solution is set to 1, is shown in Figure II.C.3. After introducing ultrapure water and the 0.5% TMAH solution for approximately 120 seconds (equivalent to the analysis of four samples), the relative intensity at *m/z* 127 was $1.6 \times 10^{-4}$. Subsequently, after introducing the 0.5% TMAH solution for a total of ~240 seconds (equivalent to the analysis of eight samples), the relative intensity at *m/z* 127 was $8.8 \times 10^{-5}$, indicating a gradual decrease in the relative intensity.

[*279] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

When the cleaning solution was the 1% TMAH + 0.01% sodium sulfite solution, the relative intensity at *m/z* 127 after approximately 120 seconds (analysis of four samples) was $1.0 \times 10^{-4}$, showing a slightly better cleaning efficiency compared with the 0.5% TMAH solution.

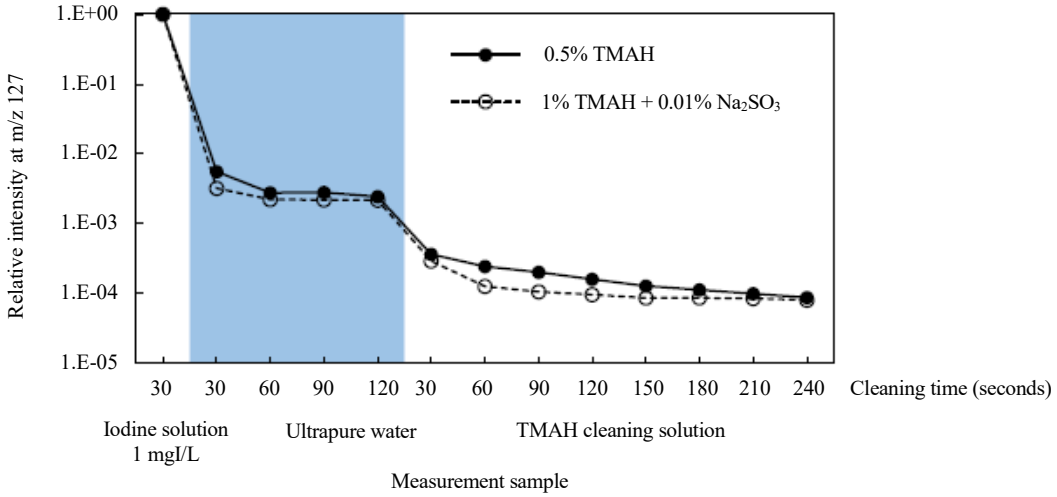



Figure II.C.3 *m/z* 127 relative Intensity as a function of the cleaning time

(3) Summary

If the relative intensity decreases to ~$10^{-4}$, it is considered that the results will not be affected when measuring samples at the same level. Therefore, sufficient cleaning effectiveness was confirmed with the cleaning conditions presented in Table II.C.1: use of the 0.5% TMAH solution for a total of 120 seconds. Since no significant improvement was observed with longer cleaning times or when using cleaning solutions with higher TMAH concentrations, 0.5% TMAH with a cleaning time of 120 seconds was selected considering operational convenience.

However, when high-iodine-concentration solutions are introduced in the system, such as samples used to confirm the $IH_2$ (ID) formation ratio, the above cleaning procedure alone is insufficient and the introduction system should be removed for cleaning.

# Explanation D Effects of Different Solvents on Iodine Determination

Well-known factors that cause changes in the sensitivity of ICP–MS include the effects of large amounts of coexisting elements (matrix interference) and changes in the ionization efficiency due to the presence of elements with low ionization energies (ionization interference). Other reported factors include the type and concentration of the solvent. Grindlay et al.[*280] reported that certain elements with high ionization energies present in carbon-containing solvents (glycerol) exhibit high sensitivity, which increases with increasing carbon concentration. Since TMAH containing carbon is used as a solvent for the measurement sample in this method, the effect of TMAH on iodine measurement was investigated.

Iodine in environmental samples exists in multiple chemical forms, such as $I^-$, $IO_3^-$, and organic iodine. It has been reported that sensitivity differences may occur between $I^-$ and $IO_3^-$ depending on the solvent. In The Series of Environmental Radioactivity Measuring Methods No. 32 "Rapid Analysis Method for Iodine-129 in Environmental Samples," it was reported that in 1 M nitric acid, $I^-$ shows higher sensitivity but larger variability whereas $IO_3^-$ shows lower sensitivity but better stability. Takaku et al.[*281] reported similar results for 1% nitric acid but no difference in sensitivity between $I^-$ and $IO_3^-$ in 1% TMAH. The sensitivity difference between $I^-$ and $IO_3^-$ has been confirmed in 0.5% TMAH in triple quadrupole ICP–MS measurements, which is the sample preparation condition for this method.

Furthermore, verification was performed to assess whether iodine measurement results differed between the sample preparation conditions of this method—using 0.5% TMAH, in which the calibration solution is present as $I^-$ while the chemical form of iodine in the measurement samples is unknown—and the ICP–MS measurement conditions described in "III. AMS," which employ 1 M nitric acid with iodine present as $IO_3^-$.

## D.1 Effect of the TMAH Concentration

(1) Verification procedure

To confirm the effect of the TMAH concentration on iodine measurement, $^{127}I$ solutions with varying TMAH concentrations were analyzed to confirm changes in the $^{127}I$ sensitivity and background signal at *m/z* 129.

1) Preparation of measurement samples
   - Here, 0, 0.1, 0.5, and 1% TMAH solutions, each spiked with potassium iodide to a concentration of 10 $\mu$gI/L, were prepared.
2) Measurement parameters
   - Measurement conditions : $^{127}I$ measurement conditions (refer to "Explanation C Example of Measurement Parameters")
   - Integration time : 1 second for *m/z* 127 and 10 seconds for *m/z* 129

[*280] G. Grindlay et al.: A systematic study on the influence of carbon on the behavior of hard-to-ionize elements in inductively coupled plasma–mass spectrometry, Spectrochimica Acta Part B: Atomic Spectroscopy, 86, 42-49 (2013)
[*281] Y. Takaku et al.: Iodine determination in natural and tap water using inductively coupled plasma mass spectrometry, Analytical Sciences, 11, 823-827 (1995)

・ Repeated measurements : Three times a day per sample for 3 days

(2) Verification results

The average counting rate and standard deviation for the 3-day measurement are shown in Figure II.D.1. At high TMAH concentrations, the *m/z* 127 counting rate increased while the *m/z* 129 background counting rate showed a slight decreasing trend.

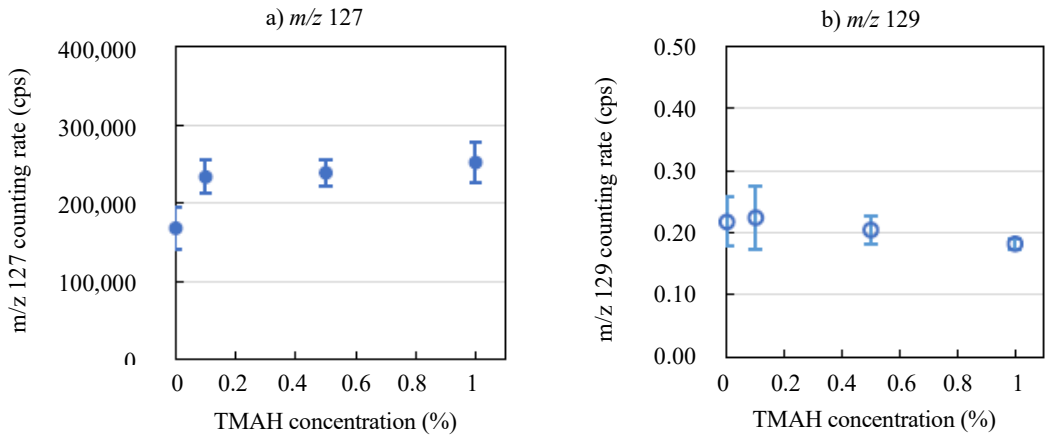



Figure II.D.1 *m/z* 127 and 129 counting rates as a function of the TMAH concentration

(3) Summary

Since the $^{127}$I sensitivity increased with increasing TMAH concentration, it is important to match the TMAH concentrations of the calibration solutions and the sample solution for accurate analysis. Increasing the TMAH concentration can improve sensitivity; however, caution is required when analyzing samples with high salt concentrations. As the basicity of the solution increases, the likelihood of salt precipitation also increases, which can reduce repeatability and signal stability.

## D.2 Sensitivity Difference Due to the Chemical Form

Using the sample preparation conditions of this method (0.5% TMAH), the sensitivity difference between $I^-$ and $IO^-$ was verified using triple quadrupole ICP–MS. In addition, the sensitivity difference of $I^-$ and $IO^-$ in pure water was examined for comparison. Measurements were also performed using a combination of 1 M nitric acid and $IO^-$, which is the ICP–MS measurement condition set in "III. AMS," to compare chemical species sensitivity and stability.

(1) Verification procedure

1) Preparation of measurement samples

・ Iodine concentration: 10 $\mu$gI/L

・ TMAH solvent: Potassium iodide or potassium iodate was dissolved in ultrapure water to prepare a solution with an iodine concentration of 10 µg/L in 0.5% TMAH.

- Ultrapure water solution: Potassium iodide or potassium iodate was dissolved in ultrapure water to obtain a final iodine concentration of 10 $\mu$g/L.
- Nitric acid solvent: Potassium iodide was dissolved in ultrapure water, after which sodium hypochlorite was added to oxidize $I^-$ into $IO_3^-$. Nitric acid was then added to prepare a solution of 1 M nitric acid with an iodine concentration of 10 $\mu$g/L.

2) Measurement parameters

- Measurement conditions : $^{127}I$ measurement conditions (refer to "Explanation C Example of Measurement Parameters")
- Integration time : 1 second for *m/z* 127.
- Repeated measurements : Three measurements per sample per day × 3 days

(2) Verification results

The counting rates of $I^-$ and $IO_3^-$ in each solvent are shown in Figure II.D.2. Regarding the effect of the chemical form on sensitivity, a difference in counting rates between $I^-$ and $IO^-$ was observed in ultrapure water; however, in the TMAH solvent, nearly identical counting rates were obtained.

Differences in the sensitivities of $I^-$ and $IO^-$ in the presence of the different solvents were observed. The sensitivities showed the following ascending order: TMAH, ultrapure water ($I^-$), nitric acid, and ultrapure water ($IO^-$). Under all conditions, the results demonstrated good repeatability and reproducibility.

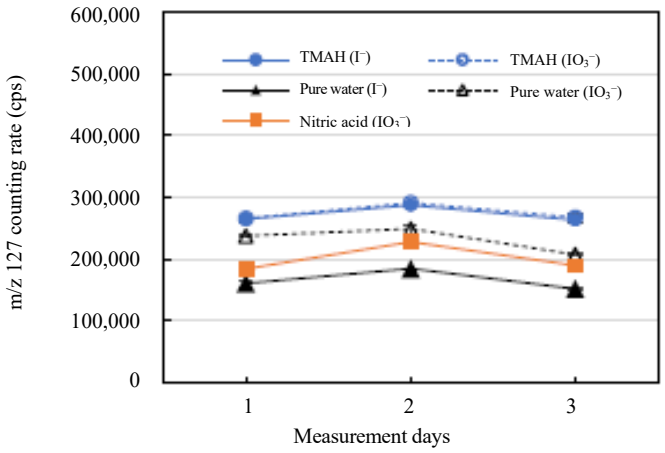



Figure II.D.2 Counting rates of $I^-$ and $IO_3^-$ in each solvent

(3) Summary

For the 0.5% TMAH solvent, no sensitivity difference between $I^-$ and $IO_3^-$ was observed in triple quadrupole ICP–MS measurements. The differing sensitivity observed in ultrapure water confirmed that sensitivity differences depend on the solvent used.

Compared to pure water and nitric acid, the use of TMAH led to a higher sensitivity of the two species, which can be explained by the sensitization effect of carbon in TMAH.

### D.3 TMAH and Nitric Acid

A comparison was conducted between the calibration and sample measurement results obtained under the sample preparation conditions of the present method (0.5% TMAH; calibration solutions in the chemical form $I^-$ and measurement samples of unknown chemical form) and those obtained under the ICP–MS measurement conditions described in "III. AMS" (1 M nitric acid; chemical form: $IO_3^-$).

#### D.3.1 Sensitivity and Linearity

(1) Verification procedure

Calibration solutions were prepared and measured according to the following procedure.

1) Preparation of calibration solutions

- Calibration solutions : (0, 0.1, 0.5, 1.0, 5.0, 10.0 $\mu$gI/L)
- TMAH : Potassium iodide was dissolved in ultrapure water to prepare calibration solutions in 0.5% TMAH.
- Nitric acid : Potassium iodide was dissolved in pure water, after which sodium hypochlorite was added to oxidize $I^-$ into $IO_3^-$. Nitric acid was then added to prepare calibration solutions in 1 M nitric acid.

2) Measurement parameters

- Measurement conditions : $^{127}$I Measurement conditions (refer to "Explanation C Example of Measurement Parameters")
- Integration time : 1 second for *m/z* 127
- Measurement date : TMAH and nitric acid were used for analysis on the same day

(2) Verification results

Calibration curves of the $^{127}$I counting rate as a function of the $^{127}$I concentration are shown in Figure II.D.3. Both solvents exhibited good linearity. Under the given conditions, the slope of the calibration curve (sensitivity) for the TMAH solvent was approximately 20% higher than that for the nitric acid solvent.

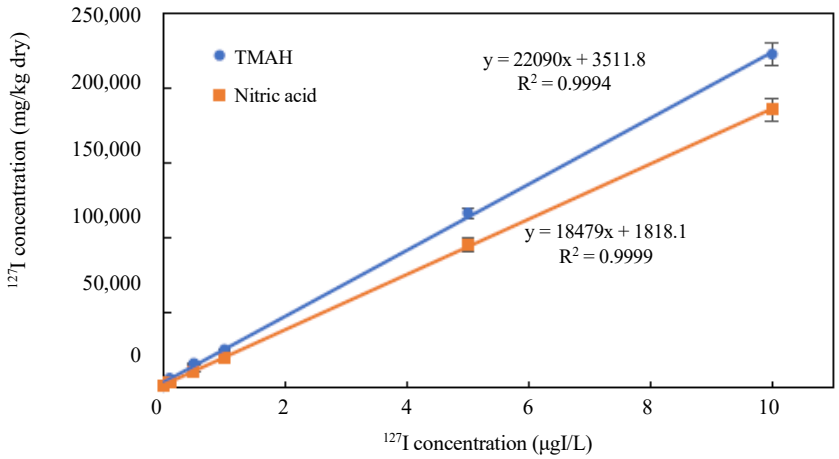



Figure II.D.3 $^{127}$I calibration curves for TMAH and nitric acid solvents

### D.3.2 Sample Measurement Result

(1) Verification procedure

Standard reference materials and environmental samples were analyzed, and the $^{127}I$ determination results of measurement samples prepared in 0.5% TMAH and 1 M nitric acid were compared.

1) Preparation of measurement samples

- TMAH solvent : An appropriate portion was aliquoted from the original sample solution (iodine trapping solution or seawater) and prepared as a 0.5% TMAH solution.
- Nitric acid solvent : An appropriate portion was aliquoted from the same original sample solution used in the case of the TMAH solvent. After addition of sodium hypochlorite, the solution was prepared as a 1 M nitric acid solution.
- Calibration solutions : Solutions with iodine concentrations of 0, 0.1, 0.5, 1.0, 5.0, 10.0 $\mu$g/L were prepared in the same solvent as that used for preparing the sample solution.
- Internal-standard elements : Rhenium for the TMAH solvent and indium for the Nitric acid solvent.

2) Measurement parameters

- Measurement conditions : $^{127}I$ measurement conditions (refer to "Explanation C Example of Measurement Parameters")
- Integration time : 1 second for *m/z* 127 and 1 second for the internal-standard element.
- Repeated measurements : Standard reference materials: 1 sample measured for 3 days
  : Environmental samples: 1 sample measured for 1 day

(2) Reference materials

1) Verification samples

The National Institute of Standards and Technology (NIST) standard reference materials used in this verification are listed in Table II.D.1.

Table II.D.1 Standard reference materials used in the verification of the effects of TMAH and nitric acid solvents

| Reference material | Sample | $^{127}I$ concentration (mg/kg dry matter) | Variation (mg/kg dry matter) | Remarks |
|---|---|---|---|---|
| NIST SRM 3232 | Kelp powder | 944 | 88 (k = 2) | Certified value |
| NIST SRM 1547 | Peach leaves | 0.3 | -※1 | Reference value |

※1 Analysis of 22 samples at the Japan Chemical Analysis Center[*282] resulted in a standard deviation of 0.02.

2) Verification results

[*282] The analysis was performed as described in "Chapter 4 Seaweed" and "Chapter 7 Measurement" ("7.1 Determination of $^{127}I$ by ICP–MS") of "III. AMS."

The results of measurements of the standard reference materials when using TMAH and nitric acid as the solvent are shown in Figure II.D.4. For both solvents, the results were within the range of variability.

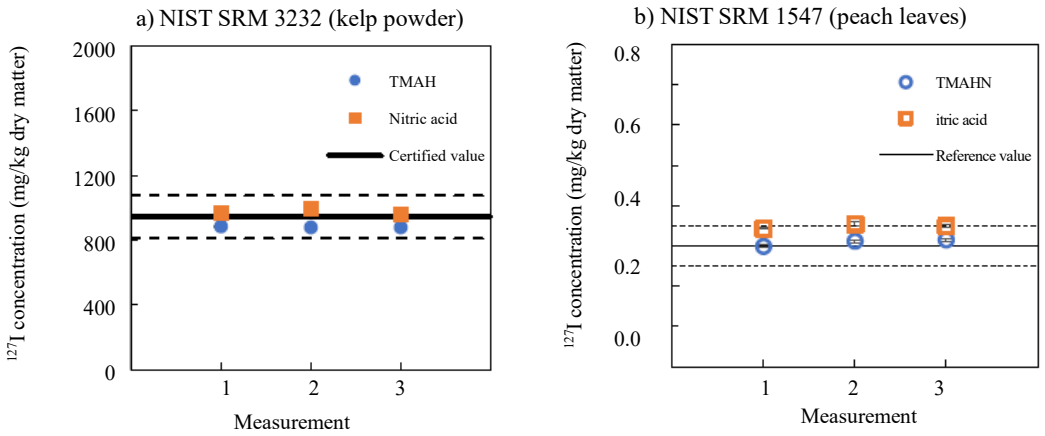



Figure II.D.4 Comparison of the measurement results for the standard reference materials

a) Results are obtained by measuring one sample over three days. The indicated range represents the uncertainty (k = 3).

b) Results are obtained by measuring one sample over three days. The range shown represents three times the standard deviation of the analytical results obtained at JCAC (number of samples: 22).

(3) Environmental samples

1) Verification samples

The following seawater and seaweed samples were used for verification.

- Seawater samples : Six samples of seawater collected off the coast of Fukushima Prefecture
- Seaweed samples : Kelp, sea lettuce, Arame, and Harigane

2) Verification results

Figure II.D.5 shows the measurement results obtained when using TMAH or nitric acid as the solvent, both of which showed good agreement.

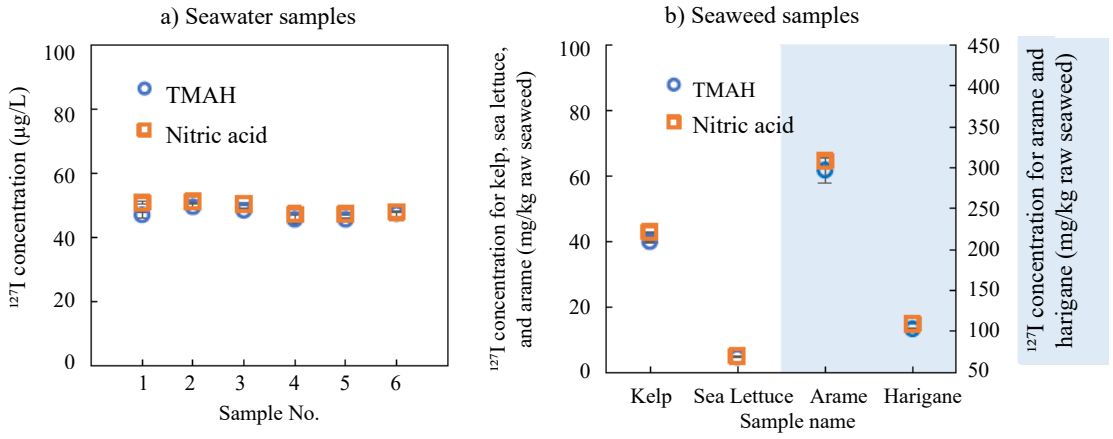



Figure II.D.5 Comparison of measurement results for different environmental samples

### D.3.3 Summary

The sample preparation condition of this method (involving the use of the 0.5% TMAH solution) led to good linearity. Measurements of standard reference materials yielded results within the range of variability. Further, measurement results of the environmental samples were in good agreement with the ICP–MS measurement results described in “III. AMS.” These findings confirm that 0.5% TMAH is suitable as a solvent for iodine analysis using triple quadrupole ICP–MS.

# Explanation E Selection of Internal-Standard Elements

While the internal-standard correction method is effective in reducing nonspectral interferences, accurate correction is achieved only when the behavior of the analyte element closely resembles that of the internal-standard element. A study was hence conducted to identify the optimal internal-standard element for $^{129}I$ analysis.

## E.1 Selection of Candidate Elements

It is essential that the internal-standard element exhibits no spectral interference with the analyte and is compatible with the solvent used for preparing the measurement sample solution. It is also desirable to select an element that behaves similarly to the target element, is identical in mass, and is present at a sufficiently low concentration in the measurement sample. Having a similar ionization potential is also advantageous.

Initially, elements commonly used for $^{127}I$ determination and elements that can be used in alkali solutions were selected. The results of this selection are presented in Table II.E.1.

Indium, which is often used as an internal-standard element in $^{127}I$ determination when using nitric acid as the solvent, cannot be used under alkaline conditions and causes interference at *m/z* 129; hence, it was excluded from consideration. Similarly, tellurium, which is used as an internal-standard element for iodine analysis as per the Analytical Manual for Standard Tables of Food Composition in Japan[*283], was excluded because it interferes at m/z 129.

As a result, gallium, rhodium, cesium, and rhenium were selected as candidates for evaluation in this study.

**Table II.E.1 Candidate internal-standard elements**

| Candidate element | Chemical symbol | Candidate mass number | Mass difference with respect to $^{129}I$ | First ionization potential (eV) | Difference in the first ionization potential with respect to I (eV) | Interference at *m/z* 129 | Remarks |
|---|---|---|---|---|---|---|---|
| Gallium | Ga | 71 | -58 | 6.00 | -4.45 | - | |
| Rhodium | Rh | 103 | -26 | 7.46 | -2.99 | - | |
| Indium | In | 115 | -14 | 5.79 | -4.66 | $^{113}In^{16}O$ | Not usable under alkaline conditions |
| Tellurium | Te | 125 | -4 | 9.01 | -1.44 | $^{128}Te^{1}H$ | |

[*283] 文部科学省 科学技術・学術制作局政策課資源室: 日本食品標準成分表2015 年版(七訂)分析マニュアル (第2章 無機質) (https://www.mext.go.jp/a_menu/syokuhinseibun/1368931.htm)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cesium | Cs | 133 | 4 | 3.89 | -6.56 | - | |
| Rhenium | Re | 185 | 56 | 7.83 | -2.62 | - | |
| **Iodine** | **I** | **129** | **-** | **10.45** | **-** | **-** | |

## E.2 $^{129}$I Addition Test for the Selection of the Internal-Standard Element

(1) Verification procedure

Seawater and freshwater samples were diluted, while seaweeds, soil samples, vegetables, milk samples, and airborne particulate matter were subjected to thermal hydrolysis. Measurement samples spiked with $^{129}$I were prepared using different dilution factors. Several candidate internal-standard elements were introduced by online addition and measured under the following conditions.

1) $^{129}$I standard solution

- $^{129}$I standard solution (41.7 ± 1 Bq/g)

2) Amount added

- $^{129}$I: 30–300 pg (200–2000 $\mu$Bq; concentration in the measurement solution: 20 mBq/L)

3) Measurement conditions

- Calibration curve : Calibration solutions prepared as per "3.1 Preparation of Calibration Solutions" of "Chapter 3 Measurement"
- Internal-standard elements : Gallium, rhodium, cesium, and rhenium
- Method of internal-standard addition : Online
- Measurement conditions : $^{129}$I measurement conditions (refer to "Explanation C Example of Measurement Parameters")
- Integration time : 10 seconds for m/z 129 and 1 second for the internal-standard elements

4) Verification samples

- Seawater and freshwater: Samples and the 25% TMAH solution were stored in separate volumetric flasks. Measurement samples prepared in 0.5% TMAH and spiked with $^{129}$I were obtained using different dilution factors.
- Seaweed (red algae), soil samples, vegetables (cabbage), milk samples, and airborne particulate matter: Seaweed was treated according to Chapter 2, and soil samples, vegetables, milk samples, and airborne particulate matter were treated via thermal hydrolysis according to "III. AMS." Measurement samples in 0.5% TMAH were prepared by aliquoting the collection solution, applying different dilution factors, and spiking with $^{129}$I.

(2) Verification results

The ratios of the measured values to the addition values are shown in Figure II.E.1. Without internal-standard correction, the measured values were generally 10%–20% higher than the addition values. For rhodium, the measured values were higher than the addition values for

multiple samples. Gallium, cesium, and rhenium yielded similar results, which were good and close to the addition values. For these three elements, samples with low dilution factors showed measured values approximately 5%–10% lower than the addition values.

Rhenium showed the best overall performance.

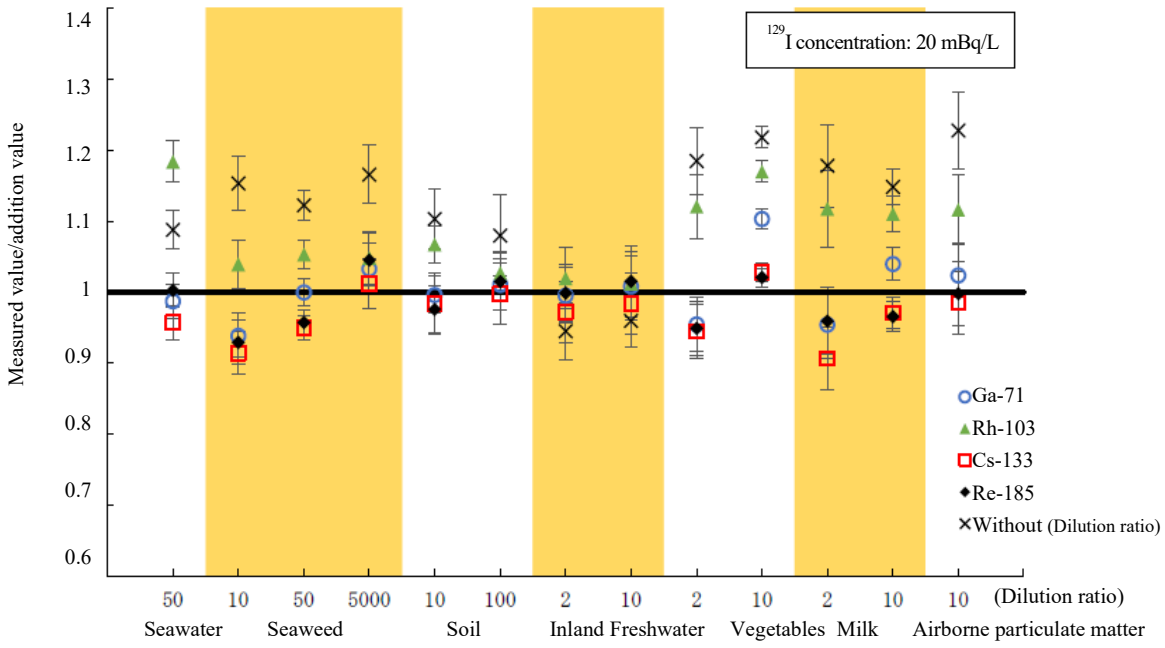



Figure II.E.1 Results of $^{129}$I addition tests obtained when using different internal-standard elements

## E.3 Verification Using Rhenium as the Internal-Standard Element

Focusing on standard reference materials, a $^{129}$I addition test was conducted using samples different from those used in "E.2 $^{129}$I Addition Test for the Selection of the Internal-Standard Element" to verify the suitability of rhenium as the internal-standard element.

(1) Verification procedure

$^{129}$I standard solutions, associated addition amounts, and measurement conditions were the same as those in "E.2 $^{129}$I Addition Test for the Selection of the Internal-Standard Element." However, only rhenium was examined as the internal-standard element. The following samples, which differ from those described in "E.2 $^{129}$I Addition Test for the Selection of the Internal-Standard Element," were used.

1) Verification samples

- Seawater, seaweed (NIST SRM 3232), airborne particulate matter (2 samples), and milk (NIST RM 8435): Prepared using the same procedure as in Section E.2.
- Marine sediment (IAEA-412): Prepared using the same procedure as that for soil samples described in Section E.2.

- Plant material (NIST SRM 1547): Prepared using the same procedure as that for seaweed described in Section E.2.
- Procedural blank: Prepared without a sample using the same procedure as that for seaweed described in Section E.2.
- 0.5% TMAH solution: Prepared by adding the $^{129}$I standard solution to a volumetric flask and filling to the calibration mark with the 0.5% TMAH solution.

(2) Verification results

The ratios of measured to addition values are shown in Figure II.E.2. As with the rhenium internal standard used in "E.2 $^{129}$I Addition Test for the Selection of the Internal-Standard Element," good agreement between measured and addition values was observed for samples with high dilution factors. Meanwhile, samples with low dilution factors showed a tendency for the measured values to be lower than the addition values. Since the measured values for the 0.5% TMAH solution and the procedural blank showed good agreement with the addition values even at low dilution factors, the lower measured values observed for actual samples can be explained by nonspectral interference caused by matrix effects. For samples with low dilution factors, such nonspectral interference may not be sufficiently corrected. Thus, it is desirable to dilute measurement samples by a factor of at least 50.

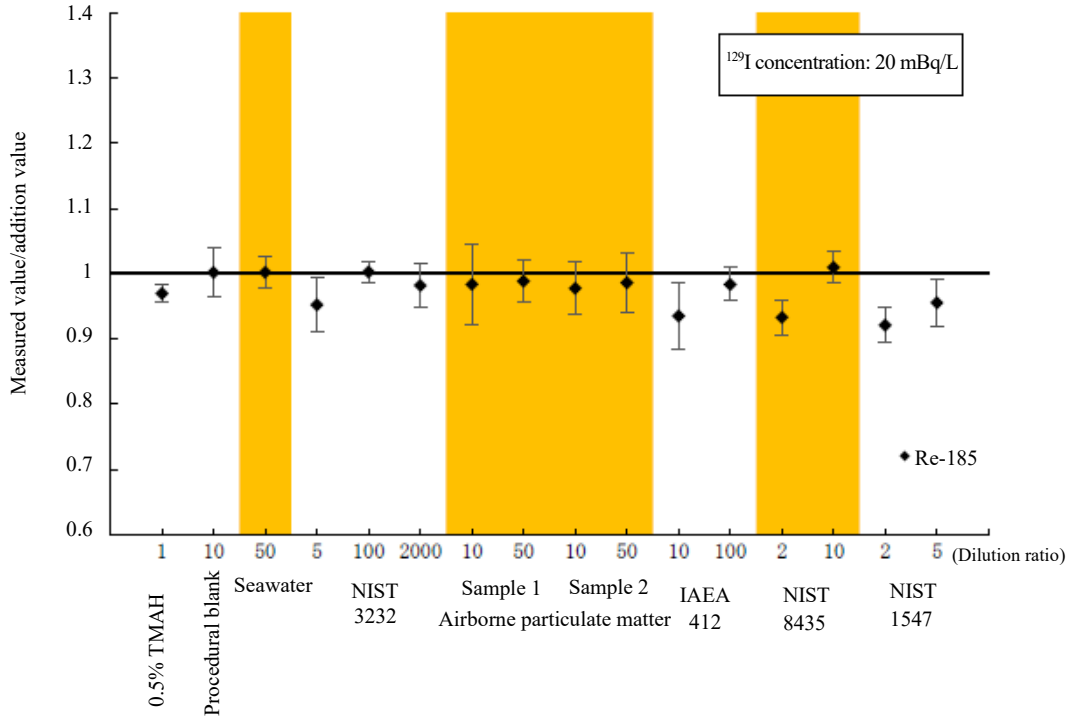



Figure II.E.2 Results of the $^{129}$I addition test when using rhenium as the internal-standard element

## Explanation F Examination of Analytical Methods for Seawater Samples

To validate the seawater analytical technique described herein, a $^{129}$I addition test was performed using seawater samples. Since the amount of the analytical sample can be increased and the detection limit can be lowered if matrix components are removed by chemical separation, the separation of iodine by solvent extraction was investigated.

### F.1 $^{129}$I Addition Test in the Dilution Measurement Method

(1) Analytical procedure

Preparation of the measurement samples was performed in accordance with "Chapter 1 Seawater Samples." Aliquots were taken from six seawater samples and added in separate volumetric flasks. Then, a $^{129}$I solution containing $^{127}$I was added up to the calibration mark. These samples were measured as per the procedure described in "3.2 Measurement Operation" of "Chapter 3 Measurement."

1) $^{129}$I solution

- tRIC-2 ($^{129}$I: 18.4 ± 0.7 Bq/kg; $^{129}$I/$^{127}$I: (3.34 ± 0.13) × $10^{-6}$)[*284]

2) Amount added

- $^{129}$I: 6 pg (40 $\mu$Bq; concentration in the measurement sample: 7 mBq/kg)
- $^{127}$I: 2 $\mu$g (concentration in the measurement sample: 300 $\mu$g/kg)

(2) Verification results

The ratios of measured to addition values of $^{129}$I and the $^{127}$I recovery rates are shown in Figure II.F.1. The $^{127}$I recovery rate was 99%–101%, which is a good result. The deviation of the measured $^{129}$I values from the addition values was 2%–5%, which is again a good result.

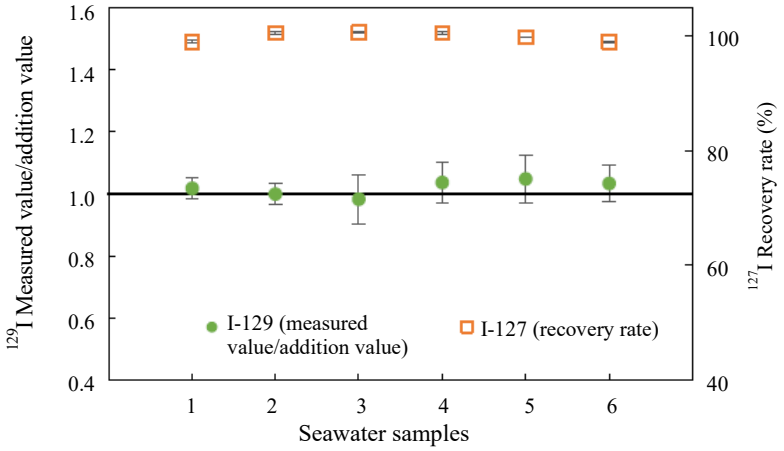



Figure II.F.1 Results of the $^{129}$I addition test in the dilution measurement method

[*284] M. Honda et al.: Preparation of Iodine-129 Standard Solutions for Triple Quadrupole ICP-MS, Journal of Nuclear and Radiochemical Sciences, 18, 1-4 (2018)

## F.2 Results of Applying the Solvent Extraction Method

### F.2.1 Analytical Procedure for the Solvent Extraction Method

(1) Verification Procedure

Solvent extraction was performed as follows (flowchart shown in Figure II.F.2):

1) A seawater sample diluted 50-fold (using the 0.5% TMAH solution) was prepared, and triple quadrupole ICP–MS measurements were performed according to the procedure described in "Explanation B Determination of $^{127}$I" to quantify $^{127}$I prior to separation.
2) Then, 100 mL of filtered seawater, 0.4 mL of 0.1 mol/L ascorbic acid, 0.8 mL of 3 mol/L hydrochloric acid, 20 mL of hexane, and 0.4 mL of 10 w/v% sodium nitrite were added to a 100 mL separatory funnel, followed by shaking. The organic and aqueous phases were then separated.
3) The aqueous phase was transferred to a 100 mL separatory funnel, 10 mL of hexane was added to it, and the resulting mixture was shaken. The organic and aqueous phases were separated. This process was repeated.
4) The obtained organic phases were combined and 2 mL of ultrapure water was added, followed by shaking.
5) To the organic phase, 5 mL of the 0.5% TMAH solution and 0.6 mL of 10 w/v% ammonium sulfite were added, followed by shaking. The resulting organic and aqueous phases were separated.
6) To the organic phase, 5 mL of the 0.5% TMAH solution and 0.2 mL of 10 w/v% ammonium sulfite were added, followed by shaking. The organic and aqueous phases were then separated.
7) The aqueous phases were combined in a beaker and concentrated by heating at 100 °C until the volume was reduced to approximately 5 mL.
8) After confirming the weight, triple quadrupole ICP–MS measurements were performed according to the procedure described in "Explanation B Determination of $^{127}$I" to determine $^{127}$I concentration. The recovery rate of $^{127}$I was calculated from the amount of $^{127}$I present before separation.
9) Triple quadrupole ICP–MS measurements were then performed according to the procedure described in "3.2 Measurement Operation" of "Chapter 3 Measurement." Further, the $^{129}$I radioactivity concentration was calculated as per "3.5.1 Calculation of $^{129}$I Radioactivity Concentration."
10) Recovery rate correction was applied, and the corrected value was taken as the measured $^{129}$I concentration in the seawater sample.

(2) Measurement conditions

$^{129}$I measurement conditions (with an axial acceleration voltage of 1.5 V) and $^{127}$I measurement conditions (refer to "C.2 Example of Measurement Parameters" in "Explanation C Example of Measurement Parameters").

(3) $^{129}$I calculation formula

$^{129}$I measured value = [$^{129}$I radioactivity concentration as per Section 3.5.1]/$^{127}$I recovery rate x 100

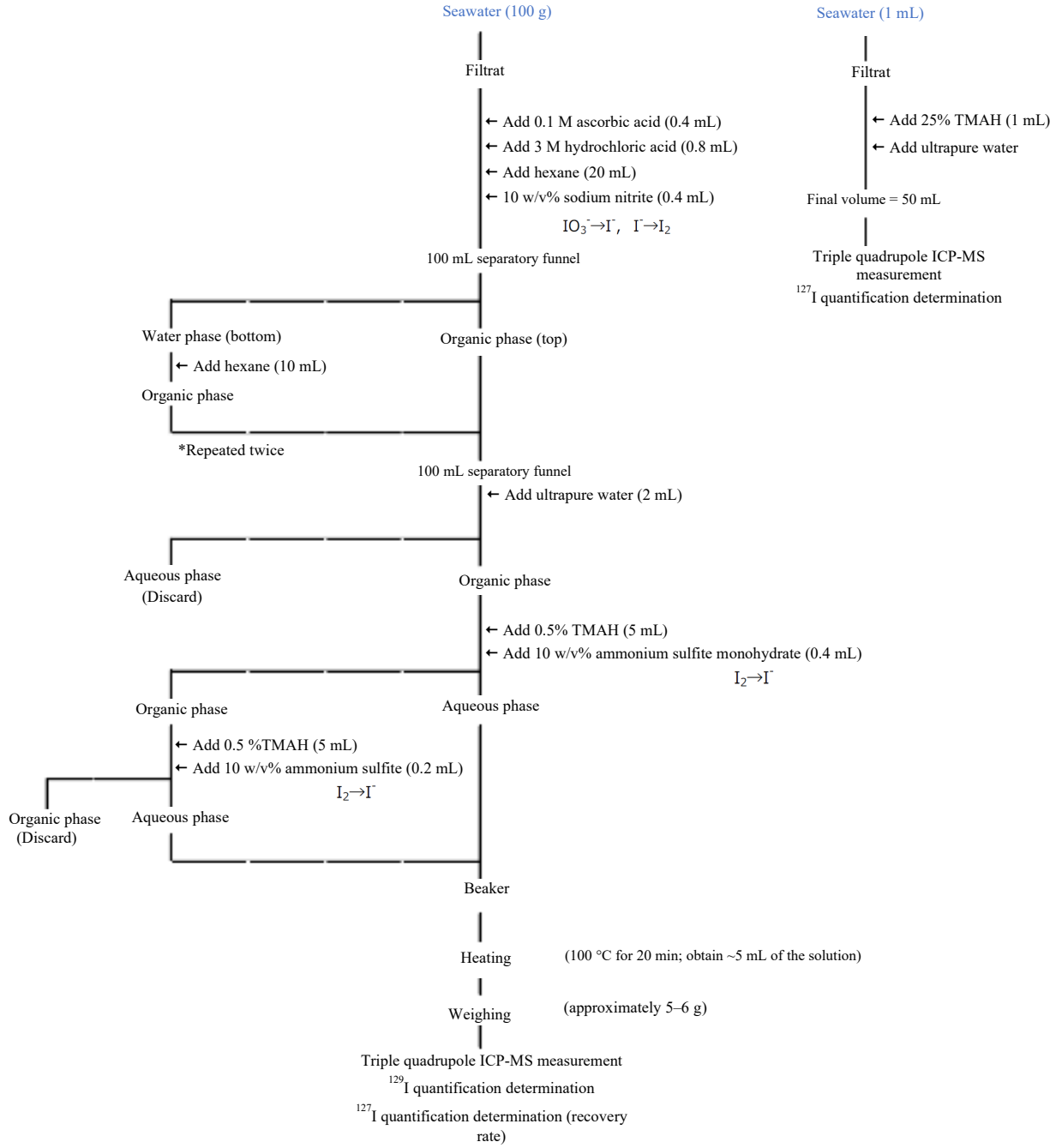



Figure II.F.2 Solvent extraction flowchart of the seawater samples

### F.2.2 $^{129}$I Addition Test

(1) Procedure

A $^{129}$I solution containing $^{127}$I was added to 100 mL of each of six seawater samples, and analysis was performed according to "F.2.1 Analytical Procedure for the Solvent Extraction Method."

1) $^{129}$I solution
   - tRIC-2 ($^{129}$I: 18.4 ± 0.7 Bq/kg; $^{129}$I/$^{127}$I: (3.34 ± 0.13) × $10^{-6}$)*285
2) Amount added
   - $^{129}$I: 17 pg (100 $\mu$Bq; concentration in 100 g of seawater: 1 mBq/kg)
   - $^{127}$I: 5 $\mu$g (concentration in 100 g of seawater: 50 $\mu$g/kg)

(2) Results

The ratio of the measured $^{129}$I concentration to the addition value and the $^{127}$I recovery rate are shown in Figure II.F.3. The $^{127}$I recovery rate was ~60%. In separation and purification, there is a known phenomenon in which the recovery rate decreases for trace elements. The concentration of $^{127}$I in seawater is ~60 $\mu$g/L, and the amount of $^{127}$I added was comparable to the amount originally present in seawater. Therefore, $^{127}$I was present at a trace level, resulting in a low recovery rate.

After correction for the $^{127}$I recovery rate, the measured $^{129}$I values were within 5% of the addition values, indicative of a good result.

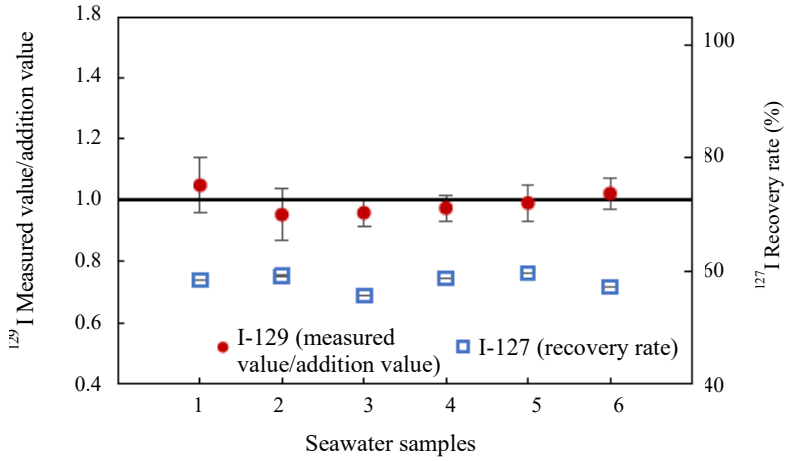



Figure II.F.3 $^{129}$I determination results obtained after solvent extraction

*285 M. Honda et al.: Preparation of Iodine-129 Standard Solutions for Triple Quadrupole ICP-MS, Journal of Nuclear and Radiochemical Sciences, 18, 1-4 (2018)

### F.2.3 Analysis of Environmental Samples

(1) Procedure

Six seawater samples were analyzed as per the procedure described in "F.2.1 Analytical Procedure for the Solvent Extraction Method."

(2) Results

The $^{127}I$ recovery rates after solvent extraction, $^{129}I$ concentration, counting rates, and calculated values of $^{127}I^{1}H_2$ ($^{127}I^{2}D$) are presented in Table II.F.1. The $^{127}I$ recovery rates ranged from 36%–52%, which were lower than those achieved in the addition test. This may be due to the fact that the environmental samples had low $^{127}I$ concentrations even though a trace amount of $^{127}I$ was added during the addition test.

The *m/z* 129 counting rates of the seawater measurement samples tended to be higher than those of the procedural blank. The calculated values of $^{127}I^{1}H_2$ ($^{127}I^{2}D$) ranged from 0.2 to 0.4 cps, suggesting that $^{127}I$ in seawater was concentrated by solvent extraction, resulting in interference from $^{127}I$ hydrides. After $IH_2$ (ID) correction, all measured $^{129}I$ values were below the lower detection limit.

Table II.F.1 Measurement results for seawater samples after solvent extraction

| Sample No. | Concentration factor | Recovery rate (%) | *m/z* 127 counting rate (cps)※1 | *m/z* 129 counting rate (cps) ※1 | Calculated $^{127}I_1H_2$ ($^{127}I^{2}D$) value (cps) ※2 | $^{129}I$ concentration (mBq/L) ※3, ※4 |
|---|---|---|---|---|---|---|
| 1 | 20 | 36 | $1.1 \times 10^7$ | 0.56 | 0.24 | <0.02 |
| 2 | 20 | 39 | $1.2 \times 10^7$ | 0.52 | 0.26 | <0.02 |
| 3 | 20 | 49 | $1.6 \times 10^7$ | 0.64 | 0.34 | <0.01 |
| 4 | 20 | 52 | $1.5 \times 10^7$ | 0.62 | 0.33 | <0.01 |
| 5 | 20 | 49 | $1.3 \times 10^7$ | 0.40 | 0.28 | <0.02 |
| 6 | 20 | 52 | $1.8 \times 10^7$ | 0.72 | 0.41 | <0.01 |
| Procedural blank | - | - | $4.2 \times 10^4$ | 0.28 | 0.00 | - |

※1 Counting rates before blank and $IH_2$ (ID) correction.

※2 The $IH_2$ (ID) formation ratio was $2.2 \times 10^{-8}$ under the measurement conditions set in this study[*286].

※3 Results after blank and $IH_2$ (ID) correction.

※4 If not detected, results are shown as "<*lower detection limit*."

[*286] Unlike the parameters in "Explanation C Example of Measurement Parameters," the measurements were performed under conditions that prioritized sensitivity, resulting in a higher $IH_2$ (ID) formation ratio.

## F.3 Detectable Levels for Seawater Samples

Table II.F.2 shows the detectable levels for the dilution measurement and solvent extraction methods as well as the calculated values of $^{127}I^{1}H_2$ ($^{127}I^{2}D$). The method for analyzing seawater should be selected according to the target lower detection limit and the acceptable complexity of the procedure.

However, since the solvent extraction method may cause interference from $^{127}I^{1}H_2$ ($^{127}I^{2}D$) due to the concentration of $^{127}I$, it is necessary to apply $IH_2$ (ID) correction. Care should be taken to confirm whether the isotopic ratio calculated from the lower detection limit and the $^{127}I$ concentration in seawater lie within the range for which the correction is applicable (i.e., above the correction applicability criterion[*287]).

Table II.F.2 Detectable levels and calculated $^{127}I1H2$ ($^{127}I2D$) values for seawater samples

| Analytical method | Concentration factor | Test quantity (mL) | Recovery rate (%) | $^{127}I^{1}H_2$ value (cps) ※1, ※2 | Detectable level (Bq/L) ※3 | Detectable isotopic ratio ※4, ※5 |
|---|---|---|---|---|---|---|
| Solvent extraction | 100 | 100 | 40 | 0.19 | $3 \times 10^{-6}$ | $(8 \times 10^{-9})$ |
| | 20 | 100 | 40 | 0.04 | $2 \times 10^{-5}$ | $4 \times 10^{-8}$ |
| | 1 | 100 | 40 | 0.002 | $3 \times 10^{-4}$ | $8 \times 10^{-7}$ |
| Dilution measurement | 0.02 | 1 | 100 | 0.0001 | $7 \times 10^{-3}$ | $2 \times 10^{-5}$ |

※1 The $^{127}I$ concentration in seawater was set at 0.06 mg/L.

※2 The sensitivity of $^{127}I$ was set at 10000 cps per 1 $\mu$g/L, and the $IH_2$ (ID) formation ratio was set at $8 \times 10^{-9}$.

※3 The lower method detection limit was set at 0.02 ng/L, and the specific activity of $^{129}I$ was set at $6.53 \times 10^{6}$ Bq/g.

※4 The isotopic ratio was calculated as (detectable level of $^{129}I$)/(concentration of $^{127}I$ in seawater).

※5 Isotopic ratios that do not meet the correction applicability criterion ($9 \times 10^{-9}$) in this measurement method are shown in parentheses.

[*287] Refer to "3.5.2 Determination of Correction Applicability" of "Chapter 3 Measurement."

# Explanation G Cross-Checking Results

## G.1 Sample for Cross-Checking

Sample : Aqueous solution spiked with $^{129}I$

Preparation : A portion (several milliliters) of the $^{129}I$ standard solution was aliquoted and transferred into a measuring flask; sodium iodide, sodium sulfite, and lithium hydroxide were added; and the flask was filled up to the calibration mark with ion-exchange water.

Distribution : The prepared solution was transferred in ampoule tubes, sealed, and distributed with each institution.

## G.2 Participating Organizations

Aomori Prefectural Nuclear Power Safety Center

Japan Atomic Energy Agency

Japan Chemical Analysis Center

## G.3 Analysis Results

Table II.G.1 shows the analysis results of each organization.

Table II.G.1 Results of sample cross-checking

| Analytical laboratory | Dilution Factor | $^{129}I$ analysis value※1 | Unit※3 |
|---|---|---|---|
| a | 10000 | 0.42 ± 0.024 | Bq/mL |
| | 50000 | 0.42 ± 0.025 | Bq/mL |
| b | 10000 | 0.42 ± 0.015 | Bq/g |
| | | 0.41 ± 0.012 | Bq/g |
| c | 10000 | 0.44 ± 0.01 | Bq/mL |
| | 20000 | 0.44 ± 0.01 | Bq/mL |
| Addition value | | 0.42 ± 0.01※2 | Bq/g |

※1 The error of the analytical values is the standard deviation obtained from repeated measurements.

※2 The error of the addition value is the uncertainty (k = 2) of the $^{129}I$ standard solution.

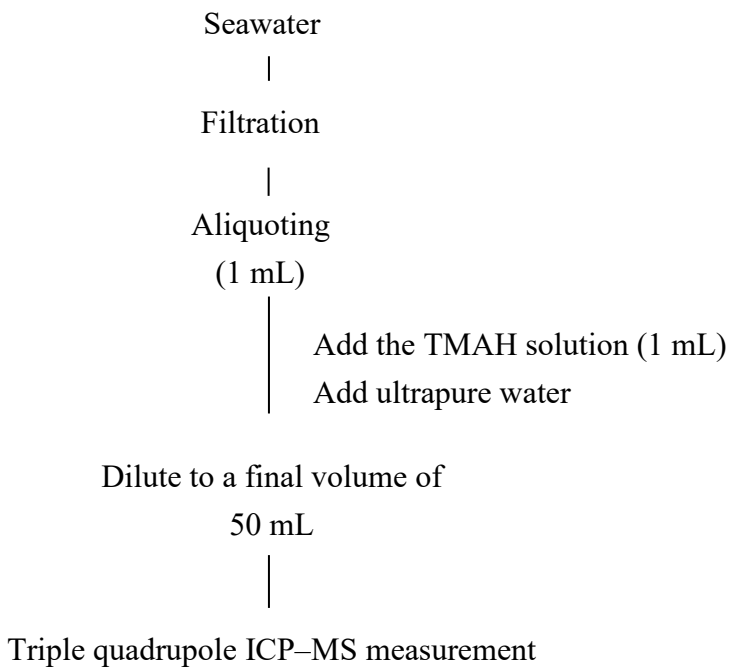
※3 The mean values and standard deviations of the results of weighing the cross-checking samples diluted 10,000-fold using a calibrated pipette (1 ml) are shown below.

1.00 ± 0.002 g/ml (10 measurements)

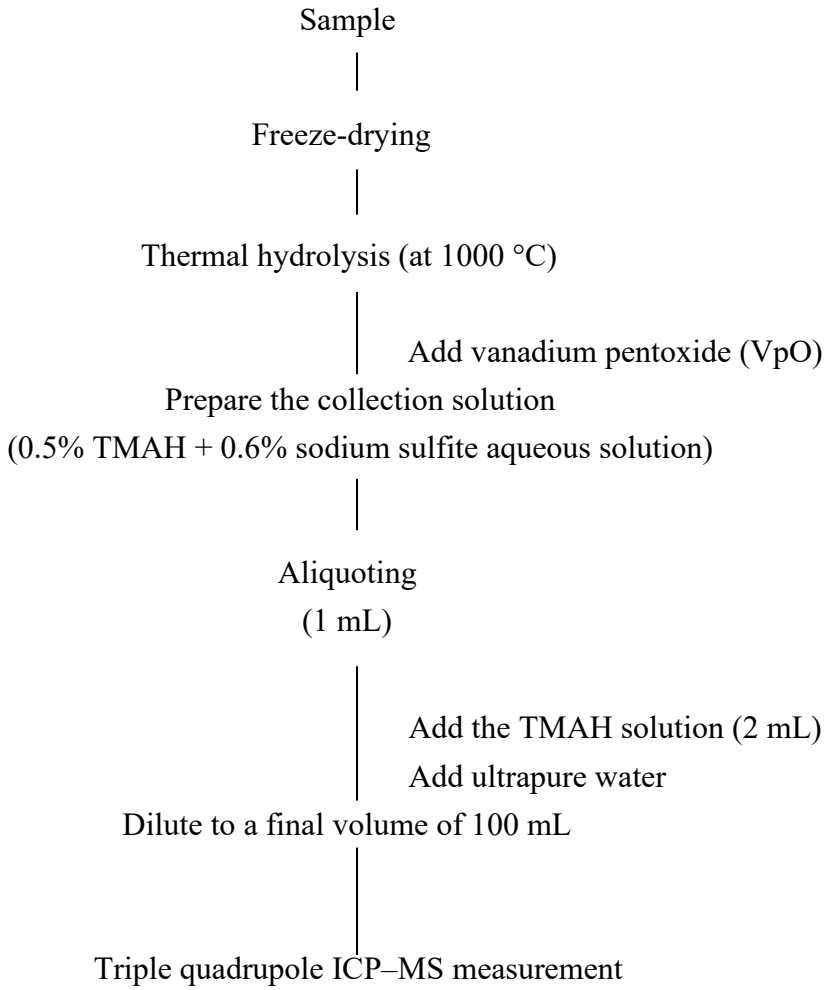
# Appendix

**Analysis Flow**

(1) Seawater



(2) Seaweed


Sample
Freeze-drying
Thermal hydrolysis (at 1000 °C)
Add vanadium pentoxide (VpO)
Prepare the collection solution
(0.5% TMAH + 0.6% sodium sulfite aqueous solution)
Aliquoting
(1 mL)
Add the TMAH solution (2 mL)
Add ultrapure water
Dilute to a final volume of 100 mL
Triple quadrupole ICP–MS measurement

# III. AMS

# Chapter 1 Airborne Particulate Matter

When analyzing airborne particulate matter, a filter paper used to collect ambient air particulates is used as the sample[*288]. The sample is thermally hydrolyzed and the released iodine is collected in a strongly alkali collection solution (Figure III.1.1). An aliquot of the resulting collection solution is taken and $^{127}I$ is measured. After aliquoting, an iodine carrier solution is added to the collection solution. Then, iodine is purified and separated via solvent extraction. A silver nitrate solution is subsequently added to form a silver iodide precipitate, from which a target for AMS measurement is prepared.

The concentration of $^{129}I$ in the sample is determined from the atomic number ratio $^{129}I/^{127}I$ obtained by AMS measurement and using the previously measured amount of $^{127}I$ contained in the sample.

## 1.1 Equipment, Instruments, and Reagents

(1) Equipment

1) Tubular electric furnace (equipped with a temperature controller and gas flowmeter; max temperature: ≥1000 °C; Figure III.1.2)
2) Electronic balance (minimum displayed value: 0.1 mg)
3) Ultrapure water production system
4) Centrifuge
5) Dryer
6) Ultrasonic cleaner

(2) Instruments

1) Quartz tubes
   - Quartz outer tube (Figure III.1.2)
   - Quartz inner tube (Figure III.1.3)
2) Bubbler tube (Figure III.1.4)[*289]
3) Quartz Wool
4) Clamp
5) Beakers (100 mL, 500 mL, and 5 L)
6) Watch glass (for a 100 mL beaker)

[*288] The amount of stable iodine ($^{127}I$) in airborne particles varies depending on the collection site and weather conditions. However, the amount contained in 1,000 $m^3$ of air is ~0.002 mg at most.
[*289] JIS standard G2, ISO standard P40 (pore size specification: 40–50 $\mu m$).

7) Volumetric flasks (25 mL, 50 mL, and 100 mL)
8) Separatory funnel (100 mL)
9) 50 mL plastic centrifuge tubes
10) 26 mL snap tubes
11) Water bath
12) Fluoroplastic tape
13) Spatulas and stainless steel spoons
14) Micro spatula
15) CB boat (or half-split quartz glass): 15 mm × 13 mm × 90 mm
16) Agate mortar
17) Desiccator
18) 3 mL glass microtubes
19) Micropipettes (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
20) Pipette tips (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
21) Glass rod
22) Aluminum foil
23) Infrared lamp
24) Hot plate
25) Gas burner
26) Desiccator

(3) Reagents

The mass and volume figures provided here are examples of preparation ratios and may be adjusted as necessary during actual preparation. Reagents conforming to the JIS should be used. For nonstandard reagents, those with the highest possible purity should be used.

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*290,*291] in 100 mL of ultrapure water.
2) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of ultrapure water.

[*290] Classified as Class 1 Hazardous Materials (Oxidizing Solids) 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.

[*291] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures must be undertaken to reduce exposure concentrations, such as by installing local exhaust ventilation systems.

3) Nitric acid (1 + 13): Mix 1 part of nitric acid[*292 *293 ,*294] (mass fraction: 60%–61% (~13 mol/L); density: 1.38 g/mL; used for measuring toxic metals) with 13 parts of ultrapure water.
4) Iodine carrier solution (10 mgI/mL): Dry approximately 3 g of potassium iodide[*292,*295] at 110 °C for 3 hours and then cool in a desiccator for 1 hour. Weigh 1.308 g and dissolve in ~50 mL of ultrapure water. Transfer to a 100 mL volumetric flask previously filled with 0.2 mL of the sodium sulfite solution (10 w/v%) and add ultrapure water up to the calibration mark of the volumetric flask. Store the solution in a cool, dark place.
5) Silver nitrate solution (10 mgAg/mL): Weigh 1.575 g of silver nitrate[*292,*293], dissolve in ultrapure water, transfer to a 100 mL volumetric flask, and dilute up to the calibration mark with ultrapure water.
6) Xylene[*295,*296,*297,*296]
7) Acetone[*295,*296,*299]
8) Methanol[*295,*296,*299]
9) Ammonia water[*291,*297,*298] (mass fraction: 28.0%–30.0%)
10) TMAH solution[*295,*296,*299] (mass fraction: 25%)
11) Sodium hypochlorite (effective chlorine content of 4% or more; food additive grade)
12) Gases
    ・Oxygen gas (purity ≥ 99.999%)
    ・City gas or propane gas
13) Niobium powder[*296]

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[*292] Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act (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 shall ensure that workers are informed of and educated in the safe handling of such substances.

[*293] Substances subject to the Poisonous and Deleterious Substances Control Act (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.” Further, appropriate measures must be undertaken to prevent theft, loss, leakage, and similar incidents.

[*294] Store in a cool, dark place. Depending on storage conditions, some iodine may be released; hence, long-term storage should be avoided.

[*295] Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act (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 shall ensure that workers are informed of and educated in the safe handling of such substances.

[*296] Substances subject to the Poisonous and Deleterious Substances Control Act (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.” Further, appropriate measures must be undertaken to prevent theft, loss, leakage, and similar incidents.

[*297] Designated as a Class II Substance under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (materials associated with chronic health effects such as carcinogenicity but not classified as Class I Substances). Exposure reduction measures are necessary, including the installation of local exhaust ventilation systems.

[*298] Refers to the guidelines issued by the Ministry of Health, Labour and Welfare under Article 28, Paragraph 3 of the Industrial Safety and Health Act, which are intended to prevent health hazards arising from chemical substances. Measures should be taken to reduce exposure to target substances.

[*299] Classified as a Class IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Following precautions are necessary: Open flames must be strictly avoided. Store and handle the material below its flash point. Ensure separate storage from Category I and Category V Hazardous Substances. Implement measures to avoid static electricity generation. When transferring to smaller containers, avoid filling to full capacity to prevent potential rupture due to thermal expansion.

14) Vanadium pentoxide[*295,*296,*297]

15) Ultrapure water (purified to a resistivity of 18 MΩ·cm or higher)[*300]

[*300] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

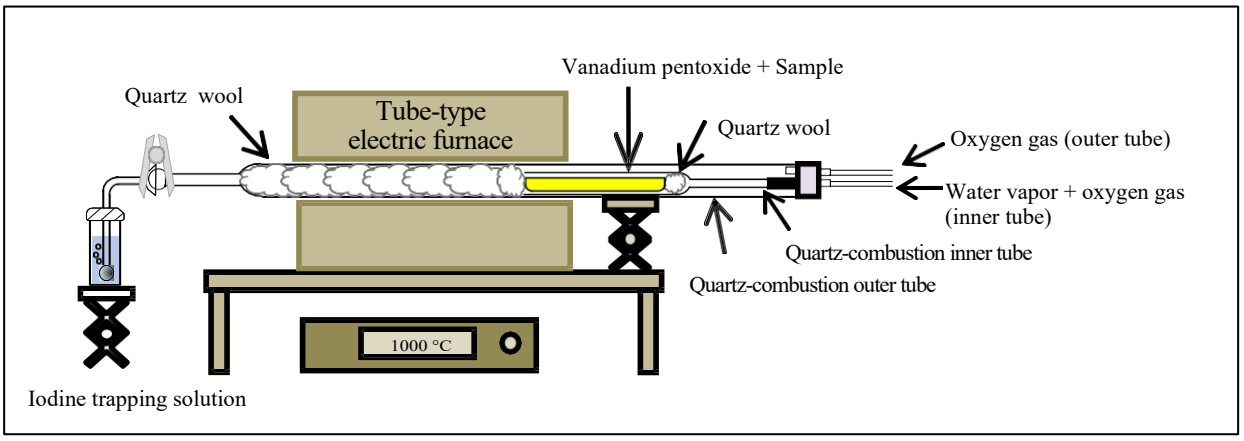



Figure III.1.1 Analytical apparatus for thermal hydrolysis

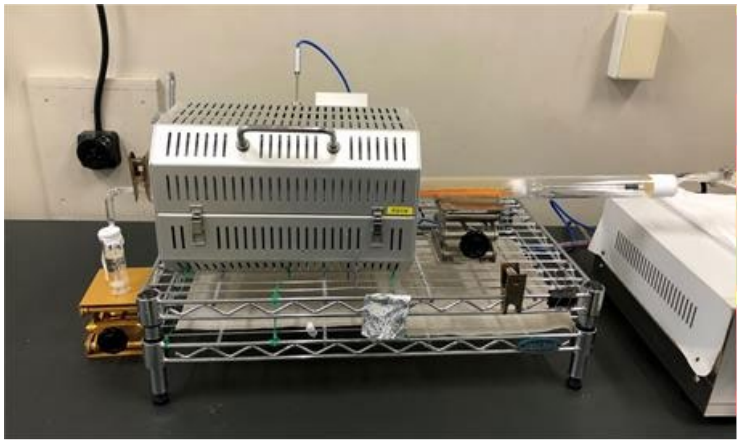


Figure III.1.2 Tubular-type electric furnace

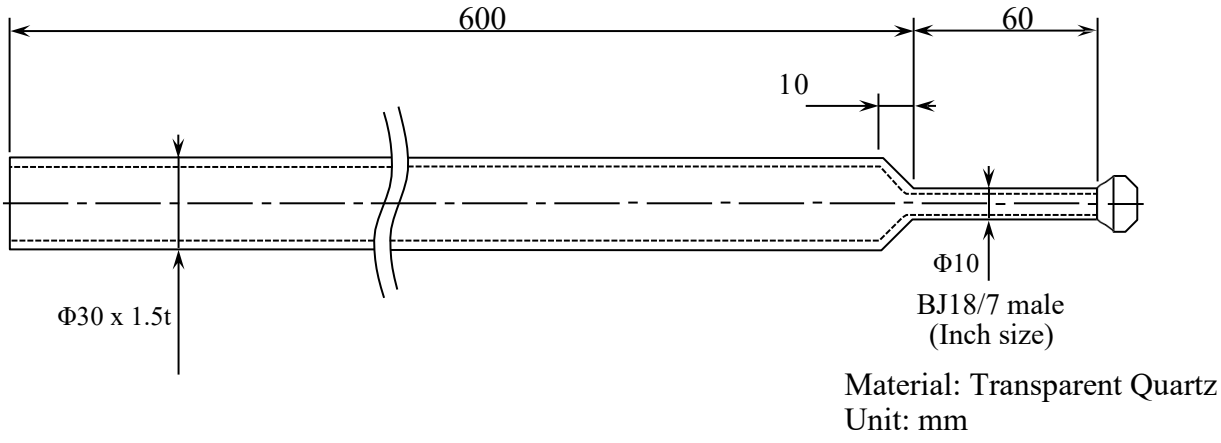
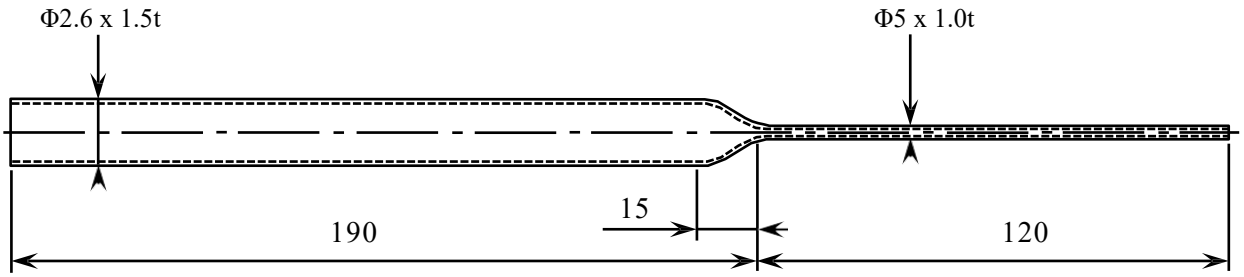
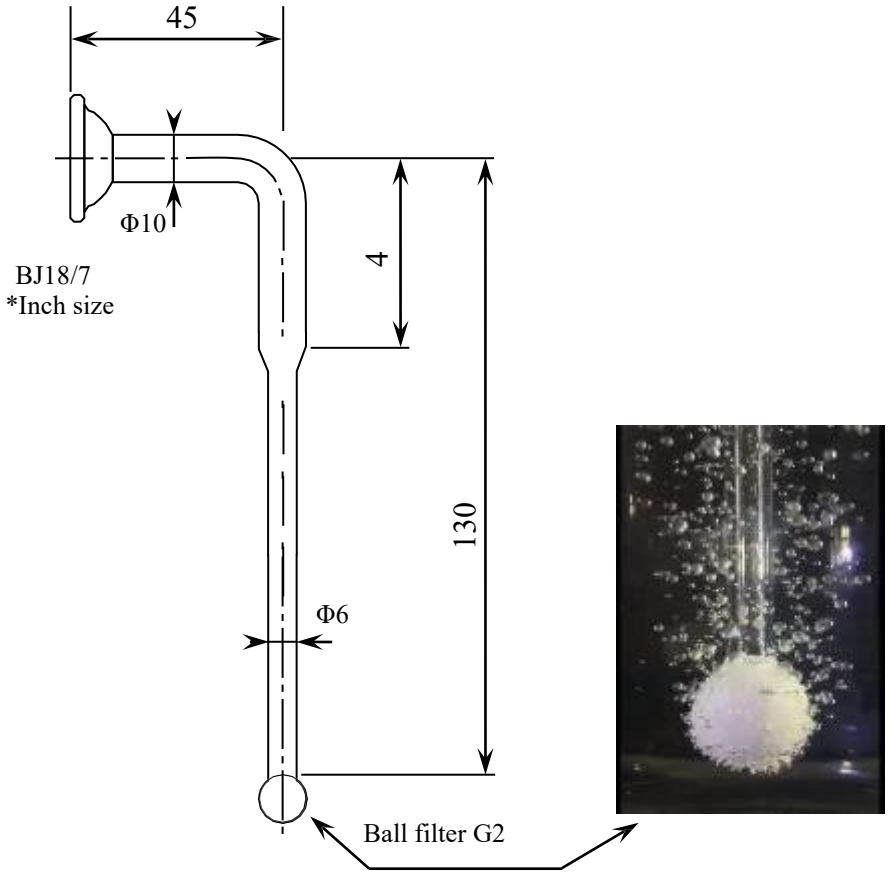



Figure III.1.3 Quartz outer tube




Material: Transparent quartz
Unit: mm

Figure III.1.4 Quartz inner tube




Material: Transparent quartz
Unit: mm

Figure III.1.5 Bubbler tube

## 1.2 Analytical Operations

### 1.2.1 Analysis and Sample Pretreatments

(1) Glassware

1) Wash glassware with acetone, ethanol, and pure water.
2) Place the glassware mentioned in Step 1) and nitric acid (1 + 13) into a 5 L beaker, cover with a watch glass, and heat until the solution boils.
3) Boil the solution for 1 hour.
4) Stop heating and allow the solution to cool to room temperature.
5) Rinse the glassware with ultrapure water and dry in a dryer at 110 °C overnight[*301].

(2) CB boat (or half-split quartz glass)

1) Place the CB boat and ultrapure water in the 500 mL beaker and clean in an ultrasonic cleaner for 30 minutes[*302].
2) Discard the ultrapure water in the beaker and repeat Step 1) three times.
3) Discard the ultrapure water in the beaker, add acetone, and rinse the beaker using an ultrasonic cleaner for 10 minutes.
4) Remove the CB boat using tweezers, place in a washed 500 mL beaker, and dry at 80 °C overnight.

(3) Blank firing of the outer tube, inner tube, and CB boat

1) Pack the quartz outer tube and inner tube with quartz wool.
2) Load the cleaned CB boat into the inner tube, insert this tube into the outer tube, and install the outer tube in the tubular electric furnace, aligning the right end of the CB boat with the furnace position[*303].
3) Connect the outer and inner tubes to oxygen gas lines and adjust the oxygen flow rates to 11.0 mL/min for the inner tube and 12.0 mL/min for the outer tube.
4) Turn on the tube-type electric furnace, heat it to the set temperature of 1000 °C, and maintain in this state for 30 minutes.
5) Move the outer tube ~10 cm to the right[*304].
6) After confirming that the temperature of the tube-type electric furnace is 1000 °C, maintain in this state for 30 minutes.

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[*301] When cleaning a volumetric flask, soak it in nitric acid (1 + 13) for 24 hours and rinse with ultrapure water.
[*302] During ultrasonic cleaning, heat is generated inside the cleaner. Hence, place ice water in the ultrasonic bath.
[*303] When closing the lid of the tubular-type electric furnace, install the CB boat so that it is not visible.
[*304] In the case of the combustion outer tube shown in Figure III.1.3, the entire outer tube must be moved 4–5 times for complete blank firing.

7) Move the outer tube and blank fire the entire tube while repeating Steps 5) and 6).
8) After the blank firing of the entire outer tube is completed, turn off the furnace, stop the oxygen gas flow, and wait until the outer tube cools to room temperature.
9) With the CB boat still inside the inner tube, cover both ends of the outer tube with aluminum foil.

(4) Sample pretreatment

1) Place the filter paper used to collect airborne particles in a drying oven, dry for 5 hours at 60°C, weigh the filter paper, and convert the weight to the cumulative air volume ($m^3$ per gram of dry filter paper).
2) Transfer the filter paper in a plastic container, pulverize it using a spatula or similar tool, and use it as the sample for iodine analysis.

### 1.2.2 Iodine Capture by Thermal Hydrolysis

(1) Preparation of the iodine-absorbing solution

1) Weigh the empty snap tube.
2) Using a micropipette, add the following to the snap tube in the given order: 8 mL of ultrapure water, 0.36 mL of the TMAH solution, 1 mL of the sodium sulfite solution (10 w/v%), and 8 mL of ultrapure water. This solution is used as the $^{129}$I-absorbing solution.

(2) Weighing of samples and preparation for combustion

1) Weigh 1–2 g of vanadium pentoxide and place half of this amount into a CB boat.
2) Weigh 1.0 g of the sample and place it on top of the CB boat.
3) Cover the sample on the CB boat with remaining vanadium pentoxide, thus sandwiching the sample between layers of vanadium pentoxide.
4) Place this structure in the inner tube.
5) Apply grease to the sliding portion of the outer tube, connect the bubbler tube and the outer tube, and fasten with a clamp.
6) Place the bubbler tube in the snap tube containing the iodine-absorbing solution prepared as per “(1) Preparation of the iodine-absorbing solution” and cover with fluoroplastic tape.
7) Insert the assembly mentioned in Step 4) into the assembly prepared in Step 5).
8) Connect the inner and outer tubes to the oxygen gas line and adjust the oxygen flow rate to 11.0 mL/min for the inner tube and 12.5 mL/min for the outer tube.
9) Confirm that bubbles are released from the bubbler tube mentioned in Step 6). If bubbles do not appear, check the connection points.

(3) Thermal hydrolysis

1) Switch on the water bath[*305]. Turn on the tubular-type electric furnace, set the temperature of the furnace to 1000 °C, and heat the furnace.
2) Once the furnace temperature reaches 1000 °C, move the outer tube into the furnace at a rate of 1 cm every 3 minutes[*306] to thermally decompose the sample. After the CB boat has completely entered the furnace, hold for 15 minutes[*307].
3) Move the outer tube from inside the furnace toward its tip at a rate of 2 cm/1.5 min and heat. After reaching the end, hold for ~5 minutes[*308].
4) Turn off the furnace and remove the bubbler tube and snap tube from the outer tube.
5) Using paper wipes moistened with acetone and ethanol, wipe off the grease applied to the outer quartz tube and bubbler tube[*309].
6) Using a micropipette, wash the inside and outside of the bubbler tube with 0.14 mL of the TMAH solution, followed by washing with 4 mL of ultrapure water. Add the cleaning solution to the snap tube containing the iodine-absorbing solution.
7) Weigh the snap tube and calculate the weight of the iodine-absorbing solution.
8) Seal the snap tube containing the iodine-absorbing solution by wrapping fluoropolymer tape between the lid and the tube, and store it in a light-shielded container covered with aluminum foil.

(4) Preparation of the iodine-absorbing solution for $^{127}$I measurement

1) From the snap tube obtained in Step 8) of "(3) Thermal Hydrolysis," collect an aliquot and add in a 100 mL volumetric flask[*310].
2) Add ~0.15 mL of the sodium hypochlorite solution, and rinse any solution adhering to the inner wall of the volumetric flask with a small amount of ultrapure water. Leave it for ~15 minutes.
3) Add a small amount of nitric acid (1 + 13) to the solution from Step 2), add an indium solution (1 $\mu$gIn/mL) as an internal standard, dilute up to the calibration mark with nitric acid (1 + 13), and mix thoroughly to obtain a sample solution for measurement[*311].

[*305] When the ultrapure water in the water bath boils, switch off the water bath.
[*306] If the outer tube is moved very quickly, the temperature inside the furnace may drop. Maintain the temperature in the furnace at 1000 °C at all times.
[*307] Ensure that vanadium pentoxide and the sample are in a completely molten state before proceeding to Step 3).
[*308] Always check for air bubbles released from the bubbler tube during Steps 1)–3).
[*309] The outer tube and bubbler tube may become hot during operation; care should be taken to avoid burns.
[*310] The dilution factor should be changed according to the amount of iodine present in the sample, and the measurement sample solution should be prepared according to the measurement conditions. Typically, when the cumulative air volume is approximately 3500–4000 $m^3$, an aliquot of ~0.5 mL should be taken so that the analyte concentration falls within the 0.0–10.0 ppb calibration curve range.
[*311] Internal-standard elements may be added using the online addition method described in "II. Triple Quadrupole ICP–MS."

### 1.2.3 Iodine Purification and Preparation of AMS Measurement Samples

(1) Separation and purification of iodine (solvent extraction)

1) Add 1 mL of the iodine carrier solution (10 mgI/mL) to the solution remaining after Step 1) in "(4) Preparation of the iodine-absorbing solution for $^{127}I$ measurement" in "1.2.2 Iodine Capture by Thermal Hydrolysis." Then, transfer to a 100 mL separatory funnel containing 20 mL of xylene.
2) Add ~3 mL of nitric acid and shake to adjust the pH value to 1.
3) Add 0.5 mL of the sodium nitrite solution (10 w/v%). While releasing gases, vigorously shake the separatory funnel for 1 minute[*312].
4) After leaving to stand, transfer the aqueous phase to a new 100 mL separatory funnel containing 20 mL of xylene[*313].
5) Add 20 mL of ultrapure water to the organic phase.
6) Shake the separatory funnel to which the aqueous phase of Step 4) has been transferred vigorously for 1 minute. After leaving to stand, discard the aqueous phase and combine the organic phase with that from Step 5).
7) Add 0.5 mL of the sodium sulfite solution (10 w/v%) to the separatory funnel from Step 5). While releasing gases, shake the separatory funnel vigorously for 1 minute[*314].
8) Transfer the aqueous phase to a 50 mL beaker. Leave the organic phase in the separatory funnel, and add 20 mL of ultrapure water and 0.1 mL of the sodium sulfite solution (10 w/v%) to the funnel.
9) Shake the separatory funnel vigorously for 1 minute while releasing gases.
10) Combine the aqueous phase with that from Step 8) and discard the organic phase.
11) Concentrate the solution obtained in Step 10) on a hot plate by heating until the volume is reduced to 10–20 mL. After cooling, transfer it to a 50-mL plastic centrifuge tube and designate this as the target preparation solution[*315].

(2) Preparation of the silver iodide precipitate

1) Add ultrapure water to the target preparation solution obtained in "(1) Separation and purification of iodine (solvent extraction)" so that the final volume is approximately 30 mL. Then, add 1 mL of ammonia water and 2–5 mL of the silver carrier solution (10 mg Ag/mL)[*316] to precipitate silver iodide (AgI).
2) After visually confirming the formation of the silver iodide precipitate in Step 1), wrap the plastic centrifuge tube with aluminum foil to protect it from light. Then, centrifuge the sample.
3) Remove the supernatant using a micropipette or a similar tool, add ~30 mL of ultrapure

[*312] Iodide ions ($I^-$) are oxidized to molecular iodine ($I^2$). (The organic phase changes in color from colorless to pink.)
[*313] In addition to xylene, benzene and toluene can be used. However, appropriate safety precautions must be taken.
[*314] Molecular iodine ($I^2$) is reduced to iodide ions ($I^-$). (The organic phase changes in color from pink to colorless.)
[*315] The concentration should be adjusted as appropriate depending on the amount of iodine ions.
[*316] The amount of the silver carrier added should be three times the amount of iodine ions.

water and 1 mL of the ammonia solution, and shake vigorously and centrifuge.

4) Remove the supernatant using a micropipette, add 10 mL of ultrapure water, shake vigorously, and centrifuge.
5) Remove the supernatant solution using a micropipette, add 10 mL of ethanol, shake vigorously, and centrifuge.
6) Weigh the tare weight of the microtube.
7) After leaving to stand, remove approximately 2–3 mL of the supernatant from step 5) using a micropipette. Mix the remaining silver iodide precipitate with ethanol and transfer it to the microtube.
8) Centrifuge the microtube containing the silver iodide precipitate, remove the supernatant, and dry under an infrared lamp until ethanol has completely evaporated.
9) Weigh the microtube and calculate the weight of the silver iodide precipitate.

(3) Preparation of the AMS measurement sample

1) Weigh the microtube obtained in Step 9) of "(2) Preparation of the silver iodide precipitate" using an electronic balance and record the weight.
2) Weigh the required amount of metallic niobium powder calculated from the net weight of the silver iodide precipitate and add it to the microtube obtained in Step 9) of "(2) Preparation of the silver iodide precipitate"[*317].
3) Thoroughly homogenize the contents of the microtube obtained in Step 2), either using an agate mortar or by mixing directly within the microtube. Then, store the sample in a desiccator. This is used as the AMS target sample.

[*317] Adjust the amount of metallic niobium powder added according to the measurement conditions of the AMS facility and instrument.

# Chapter 2 Seawater

Inorganic iodine in seawater is mostly present as iodate ions ($IO_3^-$). However, near the surface, it is also present as iodide ions ($I^-$). In addition to inorganic iodine, trace amounts of iodine may be present in dissolved organic or particulate forms; however, this guideline is limited to the determination of total inorganic iodine. For this purpose, the seawater sample is filtered, and the chemical forms of iodine are converted to iodide ions ($I^-$) by treatment with a reducing agent. An appropriate amount of an iodine carrier solution is added. Then, after the separation and purification of iodine by solvent extraction, silver iodide is prepared and an AMS measurement sample (target) is obtained. The concentration of $^{129}I$ in the sample is calculated from the atomic ratio of $^{129}I/^{127}I$ in the target obtained for AMS measurement, the independently measured $^{127}I$ concentration in the sample, and the amount of carrier added[*318].

## 2.1 Equipment, Instruments, and Reagents

(1) Equipment

1) Electronic balance (minimum displayed value: 0.01 g)
2) Ultrapure water production system
3) Centrifuge
4) Dryer
5) Shaker
6) Ultrasonic cleaner
7) Vacuum pump

(2) Instruments

1) Membrane filter unit (pore size: 0.45 $\mu$m)
2) Graduated cylinders (100 mL and 1 L)
3) Beakers (100 mL, 500 mL, and 1 L)
4) Separatory funnels (1 L and 2 L)
5) Volumetric flask (100 mL)
6) Watch glass (for a 100 mL beaker)
7) 50 mL plastic centrifuge tubes
8) Fluoroplastic tape
9) Spatulas and stainless steel spoons
10) Micro spatula
11) Desiccator
12) 3 mL glass microtubes
13) Micropipettes (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)

[*318] The amount of iodine in seawater varies depending on the sampling location and depth. However, surface seawater in coastal areas around Japan currently contains approximately 0.06 mg/L of iodine.

14) Pipette tips (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
15) Glass rod
16) Aluminum foil
17) Infrared lamp
18) Hot plate
19) Gas burner
20) Desiccator

(3) Reagents

The mass and volume figures provided here are only examples of preparation ratios and may be adjusted as necessary during actual preparation. Reagents conforming to the JIS should be used. For nonstandard reagents, those of the highest possible purity should be used.

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*319,*320] in 100 mL of ultrapure water.
2) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of ultrapure water.
3) Ascorbic acid solution (2 w/v%): Weigh 2.0 g of ascorbic acid, dissolve it in ultrapure water, transfer to a 100 mL volumetric flask, and dilute up to the calibration mark with ultrapure water.
4) Nitric acid (1 + 13): Mix 1 part of nitric acid[*321,*322] (mass fraction: 60%–61% (~13 mol/L); density: 1.38 g/mL; used for measuring toxic metals) with 13 parts of ultrapure water.
5) Hydrochloric acid (1 + 4): Mix 1 part of hydrochloric acid[*320,*321,*322] (mass fraction: 35%–37%; density: 1.18 g/mL) with 4 volumes of ultrapure water.
6) Iodine carrier solution (1 mgI/mL): Dry approximately 2 g of potassium iodide[*322,*323] at 110 °C for 3 hours and cool in a desiccator for 1 hour. Weigh 0.1308 g and dissolve in ~50 mL of ultrapure water. Transfer the resulting solution to a 100 mL volumetric flask containing 0.02 mL of the sodium sulfite solution (10 w/v%) and add ultrapure water up to the calibration mark of the volumetric flask.

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[*319] Classified as Class 1 Hazardous Materials (Oxidizing Solids) 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.

[*320] Substances subject to the Poisonous and Deleterious Substances Control Act (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." Further, appropriate measures must be taken to prevent theft, loss, leakage, and similar incidents.

[*321] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures must be undertaken to reduce exposure concentrations, such as by installing local exhaust ventilation systems.

[*322] Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act (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 shall ensure that workers are informed of and educated in the safe handling of such substances.

[*323] Store in a cool, dark place. Depending on storage conditions, some iodine may be released; hence, long-term storage should be avoided.

7) Silver nitrate solution (2 mgAg/mL): Weigh 0.315 g of silver nitrate[*320,*322], dissolve in ultrapure water, transfer the resulting solution to a 100 mL volumetric flask, and add ultrapure water up to the calibration mark of the volumetric flask.
8) Hexane[*320,*324,*325]
9) Acetone[*320,*322,*326]
10) Methanol[*320,*322,*326]
11) Ammonia water[*320,*321,*322] (mass fraction: 28.0%–30.0%)
12) Sodium hypochlorite (effective chlorine content of 4% or more; food additive grade)
13) Gases
    - Oxygen gas (purity ≥ 99.999%)
    - City gas or propane gas
14) Niobium powder[*320]

## 2.2 Analytical Operations

### 2.2.1 Preparations for Analysis and Sample Pretreatment

(1) Glassware

Perform the same operations as those described in "(1) Glassware" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(2) Pretreatment of seawater samples (suction filtration)

1) Connect the vacuum pump to the membrane filter unit.
2) Turn on the vacuum pump and wash the membrane filter unit with ultrapure water and seawater in that order.
3) Introduce the seawater sample into the unit prepared in Step 2) and perform continuous filtration[*327].
4) Collect and store the filtered seawater.

### 2.2.2 Iodine Purification and Preparation of AMS Measurement Samples

(1) Preparation of the $^{127}I$ measurement sample

[*324] Category II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Category I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, are required.

[*325] Guidelines for preventing health hazards caused by chemical substances, established by the Ministry of Health, Labour and Welfare in accordance with the provisions of Article 28, Paragraph 3 of the Industrial Safety and Health Act, apply. Measures should be taken to reduce exposure to target substances.

[*326] Classified as a Category IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Use of open flames is strictly prohibited. Store and handle remain below the material flash point. Keep away from Category I and Category V Hazardous Materials. Take precautions against static electricity generation. Avoid filling containers completely when repackaging to prevent rupture due to thermal expansion.

[*327] If the filtration rate is slow during seawater processing, replace the membrane filter unit. When using a new membrane filter unit, discard the first seawater sample without collecting it.

1) From the seawater processed as per "(2) Pretreatment of seawater samples (suction filtration)," take a 1 mL aliquot and transfer it to a 100 mL volumetric flask[*328].
2) Add approximately 0.15 mL of the sodium hypochlorite solution and rinse any solution adhering to the inner wall of the volumetric flask with a small amount of ultrapure water. Leave the flask to stand for approximately 15 minutes.
3) Add a small amount of nitric acid (1 + 13) to the solution from Step 2), add an indium solution (1 $\mu$gIn/mL) as an internal standard, and then add nitric acid (1 + 13) up to the calibration mark of the volumetric flask. Shake well to obtain the measurement sample solution.

(2) Extraction and purification of iodine

1) Measure 1 L of the filtered seawater using a graduated cylinder, weigh it on a balance, and transfer it to a 2-L separatory funnel.
2) Add 2 mL of the ascorbic acid solution (2 w/v%) and 4 mL of hydrochloric acid (1 + 4), shake the 2-L separatory funnel vigorously, and allow it to stand for 1 minute[*329].
3) Add 2 mL of the iodine carrier solution (1 mgI/mL), shake the 2-L separatory funnel vigorously, and allow it to stand for 1 minute.
4) Add 100 mL of hexane and 2 mL of the sodium nitrite solution (10 w/v%), shake the separatory funnel vigorously for 1 minute while degassing, and allow it to stand for 5 minutes.
5) Transfer the aqueous phase to a new 2-L separatory funnel, and transfer the organic phase to a 1-L separatory funnel.
6) Add 20 mL of hexane to the separatory funnel containing the aqueous phase from Step 5), shake the funnel vigorously for 1 minute while degassing, and allow it to stand. Transfer the aqueous phase to another 2-L separatory funnel, and transfer the organic phase to the 1-L separatory funnel containing the organic phase from Step 5). Repeat this operation until the organic phase becomes completely colorless. Discard the final remaining aqueous phase.
7) Add 10 mL of ultrapure water to the separatory funnel containing the organic phase from Step 6), and shake the separatory funnel vigorously for 1 minute while releasing gas intermittently. After allowing it to stand for ~5 minutes, discard the aqueous phase.
8) Add 10 mL of ultrapure water and 0.1 mL of the sodium sulfite solution (10 w/v%). While venting gases intermittently, shake the separatory funnel vigorously for 1 minute. Then, transfer the aqueous phase to a 100 mL beaker[*330].

[*328] The aliquot volume of seawater should be adjusted according to the iodine concentration in the sample, and the measurement sample solution should be prepared so as to conform to the established measurement conditions.
[*329] Iodine in seawater is reduced as follows: iodate ion $IO_3^-$ → iodide ion ($I^-$).
[*330] If the organic phase does not become colorless, add an additional 0.1 mL of the sodium sulfite solution (10 w/v%) and repeat Step 8).

9) Add 10 mL of ultrapure water, shake the separatory funnel vigorously for 1 minute while releasing gases intermittently, and transfer the aqueous phase to the 100 mL beaker from Step 8).

10) Cover the beaker with a watch glass and heat it to boiling on a hot plate until the solution volume is reduced to 5–8 mL. This solution is used as the target preparation solution[*331].

(3) Preparation of the silver iodide precipitate

1) To the target preparation solution prepared in "(2) Extraction and purification of iodine," add ultrapure water so that the final volume is ~10 mL. Then, add 1 mL of aqueous ammonia and 3–5 mL of the silver carrier solution (2 mgAg/mL)[*332] to precipitate silver iodide (AgI).

2) After visually confirming the formation of the silver iodide precipitate, shield the plastic centrifuge tube from light by wrapping it with aluminum foil. Then, centrifuge the sample.

3) Remove the supernatant using a micropipette. Add approximately 10 mL of ultrapure water and 0.5 mL of ammonia water, shake vigorously, and then centrifuge.

4) Remove the supernatant using a micropipette, add 10 mL of ultrapure water, shake vigorously, and centrifuge.

5) Remove the supernatant using a micropipette, add 10 mL of ethanol, shake vigorously, and centrifuge.

6) Weigh the tare weight of the microtube.

7) After leaving to stand, remove ~2–3 mL of the supernatant using a micropipette. Mix the remaining silver iodide precipitate with ethanol and transfer it to the microtube.

8) Centrifuge the microtube containing the transferred silver iodide precipitate, remove the supernatant, and dry under an infrared lamp until ethanol has completely evaporated.

9) Weigh the microtube and calculate the weight of the silver iodide precipitate.

(4) Preparation of the AMS measurement sample

Prepare the AMS measurement sample by following the same procedure as that described in "(3) Preparation of the AMS measurement sample" in "1.2.3 Iodine Purification and Preparation of AMS Measurement Samples" of "Chapter 1 Airborne Particulate Matter Samples."

[*331] Because only a small volume of solution remains, care should be taken to prevent the sample from drying completely.
[*332] The amount of the silver carrier added should be three times the amount of iodine ions.

# Chapter 3 Soil

When analyzing soil[*333], samples are thermally hydrolyzed, and the released iodine is collected using a strongly alkali solution (Figure III.1.1). An aliquot of the resulting collection solution is used to measure $^{127}I$. After aliquoting, an iodine carrier solution is added to the remaining collection solution and iodine is separated and purified using the solvent extraction method. A silver nitrate solution is then added to form a silver iodide precipitate, from which the target for AMS measurement is prepared.

The concentration of $^{129}I$ in the sample is determined from the atomic number ratio $^{129}I/^{127}I$ obtained by AMS measurement and using the previously measured amount of $^{127}I$ in the sample.

This method is also applicable to sediment samples, including seabed soils and marine sediments.

## 3.1 Equipment, Instruments, and Reagents

(1) Equipment

1) Tubular electric furnace (equipped with a temperature controller and gas flowmeter; max temperature: ≥1000 °C; Figure III.1.2)
2) Electronic balance (minimum displayed value: 0.1 mg)
3) Ultrapure water production system
4) Centrifuge
5) Dryer
6) Ultrasonic cleaner
7) Vibration mill

(2) Instruments

1) Quartz tubes
- Quartz outer tube (Figure III.1.2)
- Quartz inner tube (Figure III.1.3)

2) Bubbler tube (Figure III.1.4)[*334]
3) Quartz wool
4) Clamp
5) Beakers (100 mL, 500 mL, and 5 L)
6) Watch glass (for a 100 mL beaker)
7) Volumetric flasks (25 mL, 50 mL, and 100 mL)
8) Separatory funnel (100 mL)
9) 50 mL plastic centrifuge tubes
10) 26 mL snap tubes
11) Water bath
12) Fluoroplastic tape
13) Spatulas and stainless steel spoons

[*333] Depending on the type of sample and sampling location, the iodine content of soil samples is approximately 0.1–0.4 mg per 100 g. It has also been reported that $^{129}I$ concentrations in soils are generally higher in surface layers than in deeper layers.
[*334] JIS standard G2, ISO standard P40 (pore size specification: 40–50 $\mu$m).

14) Micro spatula
15) CB boat (or half-split quartz glass): 15 mm × 13 mm × 90 mm
16) Agate mortar
17) Desiccator
18) 3 mL glass microtubes
19) Micropipettes (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
20) Pipette tips (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
21) Glass rod
22) Aluminum foil
23) Infrared lamp
24) Hot plate
25) Gas burner
26) Desiccator
27) Porcelain mortar and pestle
28) Heat-resistant tray

(3) Reagents

The mass and volume figures provided here are only examples of preparation ratios and may be adjusted as necessary during actual preparation. Reagents conforming to the JIS should be used. For nonstandard reagents, those with the highest possible purity should be used.

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*335,*336] in 100 mL of ultrapure water.
2) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of ultrapure water.
3) Nitric acid (1 + 13): Mix 1 part of nitric acid[*336,*337,*338] (mass fraction: 60%–61% (~13 mol/L); density: 1.38 g/mL; used for measuring toxic metals) with 13 parts of ultrapure water.
4) Iodine carrier solution (10 mgI/mL): Dry approximately 2 g of potassium iodide[*338,*339] at 110 °C for 3 hours and cool in a desiccator for 1 hour. Weigh 1.308 g and dissolve in ~50 mL of ultrapure water.

   Transfer to a 100 mL volumetric flask containing 0.2 mL of the sodium sulfite solution

[*335] Classified as Class 1 Hazardous Materials (Oxidizing Solids) under the Fire Service Act. Care should be taken to avoid contact with strong acids, storage with combustible materials, heating, impact, and friction.
[*336] Substances subject to the Poisonous and Deleterious Substances Control Act (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.” Further, appropriate measures must be taken to prevent theft, loss, leakage, and similar incidents.
[*337] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures must be taken to reduce exposure concentrations, such as by installing local exhaust ventilation systems.
[*338] Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act (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 shall ensure that workers are informed of and educated in the safe handling of such substances.
[*339] Store in a cool, dark place. Depending on storage conditions, some iodine may be released; hence, long-term storage should be avoided.

(10 w/v%) and add ultrapure water up to the calibration mark of the volumetric flask. Store the solution in a cool, dark place.

5) Silver nitrate solution (10 mgAg/mL): Weigh 1.575 g of silver nitrate[*338,*340], dissolve in ultrapure water, transfer to a 100 mL volumetric flask, and add ultrapure water up to the calibration mark.
6) Xylene[*338,*340,*341,*342]
7) Acetone[*338,*340,*343]
8) Methanol[*338,*340,*344]
9) Ammonia water[*337,*338,*340] (mass fraction: 28.0%–30.0%)
10) TMAH solution[*338,*340,*343] (mass fraction: 25%)
11) Sodium hypochlorite (effective chlorine content of 4% or more; food additive grade)
12) Gases
    - Oxygen gas (purity ≥ 99.999%)
    - City gas or propane gas
13) Niobium powder[*340]
14) Vanadium pentoxide[*338,*340,*341]
15) Ultrapure water (purified to a resistivity of 18 MΩ·cm or higher[*344])

## 3.2 Analytical Operations

### 3.2.1 Analysis and Sample Pretreatments

(1) Glassware

Perform the same operations as those described in "(1) Glassware" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(2) CB boat (or half-split quartz glass)

Perform the same procedure as described in "(2) CB board (or half-split quartz glass)" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(3) Blank firing of the outer tube, inner tube, and CB boat

Perform the same operations as those described in "(3) Blank firing of the outer tube, inner tube, and CB boat" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne

[*340] Substances subject to the Poisonous and Deleterious Substances Control Act (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." Further, appropriate measures must be taken to prevent theft, loss, leakage, and similar incidents.

[*341] Category II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Category I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, are required.

[*342] Refers to the guidelines established by the Ministry of Health, Labour and Welfare under Article 28, Paragraph 3 of the Industrial Safety and Health Act, concerning the prevention of health hazards arising from chemical substances. Measures should be taken to reduce exposure to target substances.

[*343] Classified as a Class IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Following precautions are necessary: Open flames must be strictly avoided. Store and handle the material below its flash point. Ensure separate storage from Category I and Category V Hazardous Substances. Implement measures to avoid static electricity generation. When transferring to smaller containers, avoid filling to full capacity to prevent potential rupture due to thermal expansion.

[*344] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

Particulate Matter Samples."

(4) Sample pretreatment

1) Spread the sample (wet soil) on a heat-resistant tray, measure and record the weight, place it in a drying oven, and dry at 70°C for at least 12 hours.
2) Lightly grind the dried sample obtained from Step 1) using a porcelain mortar and pestle. Sieve the sample through a 2 mm mesh while removing stones, plant roots, etc.
3) Further pulverize the sample into a fine powder using a vibration mill. Then, homogenize it to obtain the iodine analysis sample.

### 3.2.2 Iodine Capture by Thermal Hydrolysis

(1) Preparation of the iodine-absorbing solution

Perform the same operations as described in "(1) Preparation of the iodine-absorbing solution" in "1.2.2 Iodine Capture by Thermal Hydrolysis" of "Chapter 1 Airborne Particulate Matter Samples."

(2) Weighing of samples and preparation for combustion

Perform the same operations as described in "(2) Weighing of samples and preparation for combustion" in "1.2.2 Iodine Capture by Thermal Hydrolysis" of "Chapter 1 Airborne Particulate Matter Samples."

(3) Thermal hydrolysis

1) Switch on the water bath[*345]. Turn on the tubular-type electric furnace, set the temperature to 1000 °C, and heat it.
2) Once the furnace temperature reaches 1000 °C, move the outer tube into the furnace at a rate of 1 cm per 3 minutes[*346] to thermally decompose the sample. After the CB boat has completely entered the furnace, hold for 15 minutes[*347].
3) Move the outer tube within the tubular electric furnace toward the tip at a rate of 2 cm per 1.5 minutes while heating. After reaching the tip of the outer tube, hold for ~5 minutes[*348].
4) Turn off the furnace and remove the bubbler tube and snap tube from the outer tube.
5) Using paper wipes moistened with acetone and ethanol, wipe off the grease applied to the outer tube and the bubbler tube[*349].
6) Using a micropipette, wash the inside and outside of the bubbler tube with 0.14 mL of the TMAH solution and 4 mL of ultrapure water in that order. Add the cleaning solution to the snap tube containing the iodine-absorbing solution.
7) Weigh the snap tube and calculate the weight of the iodine-absorbing solution.
8) Snap tubes containing the iodine collection solution should be sealed with fluoroplastic tape

[*345] When the ultrapure water in the water bath boils, switch off the water bath.
[*346] If the outer tube is moved very quickly, the temperature inside the furnace may drop. Maintain the temperature in the electric furnace at 1000 °C at all times. In samples with a high organic content, incomplete combustion may cause tar to adhere to the bubbler side.
[*347] Ensure that vanadium pentoxide and the sample are in a completely molten state before proceeding to Step 3).
[*348] Always check for air bubbles released from the bubbler tube during Steps 1)–3).
[*349] The outer tube and the bubbler tube may be hot; therefore, care should be taken to avoid burns.

wrapped between the lid and the snap tube and stored in a light-shielded container covered with aluminum foil.

(4) Preparation of the iodine-absorbing solution for $^{127}I$ measurement

1) From the snap tube mentioned in Step 8) of "(3) Thermal hydrolysis," collect an aliquot and transfer in a 100 mL volumetric flask[*350].
2) Add approximately 0.15 mL of the sodium hypochlorite solution and rinse any solution adhering to the inner wall of the volumetric flask with a small amount of ultrapure water. Allow the flask to stand for approximately 15 minutes.
3) Add a small amount of nitric acid (1 + 13) to the solution from Step 2), add an indium solution (1 $\mu$gIn/mL) as an internal standard, and then add nitric acid (1 + 13) up to the calibration mark of the volumetric flask. Shake well to prepare the measurement sample solution[*351].

### 3.2.3 Iodine Purification and Preparation of AMS Measurement Samples

(1) Separation and purification of iodine (solvent extraction)

1) Add 1 mL of the iodine carrier (10 mgI/mL) to the solution remaining after Step 1) in "(4) Preparation of the iodine-absorbing solution for $^{127}I$ measurement" in "3.2.2 Iodine Capture by Thermal Hydrolysis" and transfer it to a 100 mL separatory funnel containing 20 mL of xylene.
2) Add ~3 mL of nitric acid and shake to adjust the pH level to 1.
3) Add 0.5 mL of the sodium nitrite solution (10 w/v%) and shake the separatory funnel vigorously for 1 minute while releasing gases[*352].
4) After leaving to stand, transfer the aqueous phase to a new 100 mL separatory funnel containing 20 mL of xylene[*353].
5) Add 20 mL of ultrapure water to the organic phase.
6) Shake the separatory funnel containing the aqueous phase from Step 4) vigorously for 1 minute. After leaving to stand, discard the aqueous phase and combine the organic phase with that from Step 5).
7) Add 0.5 mL of the sodium sulfite solution (10 w/v%) to the separatory funnel from Step 5). Shake the separating funnel vigorously for 1 minute while releasing gases[*354].
8) Transfer the aqueous phase to a 50 mL beaker. Leave the organic phase in the separatory funnel, and add 20 mL of ultrapure water and 0.1 mL of the sodium sulfite solution (10 w/v%) to the funnel.
9) Shake the separatory funnel vigorously for 1 minute while releasing gases.
10) Combine the aqueous phase with that obtained in Step 8) and discard the organic phase.

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[*350] The dilution factor should be adjusted according to the amount of iodine present in the sample, and the measurement sample solution should be prepared according to the measurement conditions. (Typically, soil samples should be aliquoted at approximately 0.5–1.0 mL so that the analyte concentration falls within the 0–10 ppb calibration curve range.)

[*351] The internal-standard elements may be introduced using the online addition method described in "II. Triple Quadrupole ICP–MS."

[*352] Iodide ions ($I^-$) are oxidized into molecular iodine ($I^2$). (The organic phase changes in color from colorless to pink.)

[*353] In addition to xylene, benzene and toluene can be used; however, appropriate safety precautions must be taken.

[*354] Molecular iodine ($I_2$) is reduced to iodide ions ($I^-$). (The organic phase changes in color from pink to colorless.)

11) Heat the combined solution from Step 10) on a hot plate to concentrate it to a volume of 10–20 mL. After cooling, transfer it to a 50 mL plastic centrifuge tube. This solution is used as the target preparation solution[*355].

(2) Preparation of the silver iodide precipitate

Perform the same procedure as described in "(2) Preparation of the silver iodide precipitate" in "1.2.3 Iodine Purification and Preparation of AMS Measurement Samples" of "Chapter 1 Airborne Particulate Matter Samples."

[*355] The concentration should be adjusted as appropriate depending on the amount of iodide ions.

# Chapter 4 Seaweed

When analyzing seaweeds, samples freeze-dried in advance are used for measurement. The samples are subjected to thermal hydrolysis, and released iodine is collected using a strongly alkali solution. An aliquot of the resulting collection solution is used to measure $^{127}I$. After aliquoting, an iodine carrier solution is added to the remaining collection solution, and iodine is separated and purified using the solvent extraction method. A silver nitrate solution is then added to form a silver iodide precipitate, from which a target for AMS measurement is prepared. The concentration of $^{129}I$ in the sample is calculated from the $^{129}I/^{127}I$ atomic ratio obtained by AMS measurement and the previously measured amount of $^{127}I$ in the sample.

Since the $^{127}I$ concentration in samples varies depending on the seaweed species, the amount of sample used must be adjusted as appropriate[*356].

## 4.1 Equipment, Instruments, and Reagents

(1) Equipment

1) Tubular electric furnace (equipped with a temperature controller and gas flowmeter; max temperature: ≥1000 °C; Figure III.1.2)
2) Electronic balance (minimum displayed value: 0.1 mg)
3) Ultrapure water production system
4) Centrifuge
5) Dryer
6) Ultrasonic cleaner
7) Freeze-dryer

(2) Instruments

1) Quartz tubes
   - Quartz outer tube (Figure III.1.2)
   - Quartz inner tube (Figure III.1.3)
2) Bubbler tube (Figure III.1.4)[*357]
3) Quartz wool
4) Clamp

[*356] Typical examples of iodine concentrations and dried residues in seaweeds are provided below.

| Seaweed | $^{127}I$ concentration (mg/kg raw) | Dry residue (%) |
|---|---|---|
| Amanori | 1 ～ 30 | 5 |
| Kombu | 30 ～ 1,300 | 20 |
| Hijiki | 30 ～ 530 | 20 |
| Wakame | 10 ～ 130 | 5 |

[*357] JIS standard G2, ISO standard P40 (pore size specification: 40–50 μm).

5) Beakers (100 mL, 500 mL, and 5 L)
6) Watch glass (for a 100 mL beaker)
7) Volumetric flasks (25 mL, 50 mL, and 100 mL)
8) Separatory funnel (100 mL)
9) 50 mL plastic centrifuge tubes
10) 26 mL snap tubes
11) Water bath
12) Fluoroplastic tape
13) Spatulas and stainless steel spoons
14) Micro spatula
15) CB boat (or half-split quartz glass; 15 mm × 13 mm × 90 mm)
16) Agate mortar
17) Desiccator
18) 3 mL glass microtubes
19) Micropipettes (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
20) Pipette tips (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
21) Glass rod
22) Aluminum foil
23) Infrared lamp
24) Hot plate
25) Gas burner
26) Desiccator

(2) Reagents

The mass and volume figures provided here are only examples of preparation ratios and may be adjusted as necessary during actual preparation. Reagents conforming to the JIS should be used. For nonstandard reagents, those with the highest possible purity should be used.

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*358,*359] in 100 mL of ultrapure water.
2) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of ultrapure water.

[*358] Classified as Class 1 Hazardous Materials (Oxidizing Solids) under the Fire Service Act. Care should be taken to avoid contact with strong acids, storage with combustible materials, heating, impact, and friction.
[*359] Substances subject to the Poisonous and Deleterious Substances Control Act (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.” Further, appropriate measures must be taken to prevent theft, loss, leakage, and similar incidents.

3) Nitric acid (1 + 13): Mix 1 part of nitric acid[*359,*360,*361] (mass fraction: 60%–61% (13 mol/L); density: 1.38 g/mL; used for measuring toxic metals) with 13 parts of ultrapure water.
4) Iodine carrier solution (10 mgI/mL): Dry approximately 3 g of potassium iodide[*361,*362] at 110 °C for 3 hours and then cool in a desiccator for 1 hour. Weigh 1.308 g and dissolve in ~50 mL of ultrapure water. Transfer the resulting solution to a 100 mL volumetric flask containing 0.2 mL of the sodium sulfite solution (10 w/v%) and add ultrapure water up to the calibration mark of the volumetric flask. Store the solution in a cool, dark place.
5) Silver nitrate solution (10 mgAg/mL): Weigh 1.575 g of silver nitrate[*359,*361], dissolve in ultrapure water, transfer the resulting solution to a 100 mL volumetric flask, and dilute up to the calibration mark with ultrapure water.
6) Xylene[*359,*361,*363,*364]
7) Acetone[*359,*361,*365]
8) Methanol[*359,*361,*366]
9) Ammonia water[*359,* 360,*361] (mass fraction: 28.0%–30.0%)
10) TMAH solution[*359,*361,*365] (mass fraction: 25%)
11) Sodium hypochlorite (effective chlorine content of 4% or more; food additive grade)
12) Gases
    - Oxygen gas (purity ≥ 99.999%)
    - City gas or propane gas
13) Niobium powder[*359]
14) Vanadium pentoxide[*359,*361,*363]
15) Ultrapure water (purified to resistivity of 18 MΩ·cm or higher[*366])

[*360] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures must be taken to reduce exposure concentrations, such as by installing local exhaust ventilation systems.
[*361] Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act (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 should ensure that workers are informed of and educated in the safe handling of such substances.
[*362] Store in a cool, dark place. Depending on storage conditions, some iodine may be released; hence, long-term storage should be avoided.
[*363] Category II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Category I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, are required.
[*364] Refers to the guidelines issued by the Ministry of Health, Labour and Welfare under Article 28, Paragraph 3 of the Industrial Safety and Health Act, which are intended to prevent health hazards arising from chemical substances. Measures should be taken to reduce exposure to target substances.
[*365] Classified as a Class IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Following precautions are necessary: Open flames must be strictly avoided. Store and handle the material below its flash point. Ensure separate storage from Category I and Category V Hazardous Substances. Implement measures to avoid static electricity generation. When transferring to smaller containers, avoid filling to full capacity to prevent potential rupture due to thermal expansion.
[*366] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

## 4.2 Analytical Operations

### 4.2.1 Analysis Preparation

(1) Glassware

Perform the same operations as those described in "(1) Glassware" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(2) CB boat (or half-split quartz glass)

Perform the same procedure as described in "(2) CB board (or half-split quartz glass)" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(3) Blank firing of the outer tube, inner tube, and CB boat

Perform the same operations as those described in "(3) Blank firing of the outer tube, inner tube, and CB boat" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(4) Sample pretreatment

1) After weighing the raw (moist) sample, place it in a polypropylene container and prefreeze it at −20 °C or lower for at least 36 hours.
2) Transfer the entire container to a dryer for continuous freeze-drying while maintaining a vacuum of 1 Torr or less.
3) Then, measure and record the weight and finely pulverize the dried sample. Finally, use it as the iodine analysis sample.

### 4.2.2 Iodine Capture by Thermal Hydrolysis

(1) Preparation of the iodine-absorbing solution

1) Weigh the empty snap tube.
2) Using a micropipette, add the following to the snap tube in the given order: 8 mL of ultrapure water, 0.36 mL of the TMAH solution, 1 mL of the sodium sulfite solution (10 w/v%), and 8 mL of ultrapure water. This solution is used as the iodine-absorbing solution for $^{129}I$ measurement.

(2) Weighing of samples and preparation for combustion

1) Weigh 1–1.5 g of vanadium pentoxide and place half of it in a CB boat.
2) Weigh 0.5 g of the sample and place it on top of the CB boat.
3) Cover the sample on the CB boat with the remaining vanadium pentoxide from Step 1), thus sandwiching the sample between layers of vanadium pentoxide.
4) Place this structure in the inner tube.
5) Apply grease to the sliding portion of the outer tube, connect the bubbler tube and the outer tube, and fasten with a clamp.

6) Place the bubbler tube in the snap tube containing the iodine-absorbing solution prepared in "(1) Preparation of the iodine-absorbing solution" and wrap with fluoroplastic tape.
7) Insert the assembly from Step 4) into the assembly prepared in Step 5).
8) Connect the inner and outer tubes to the oxygen gas line and adjust the oxygen flow rate to 11.0 mL/min for the inner tube and 12.5 mL/min for the outer tube.
9) Confirm that bubbles are released from the bubbler tube in Step 6). If bubbles do not appear, check the connection points.

(3) Thermal hydrolysis

1) Switch on the water bath[*367]. Turn on the tubular-type electric furnace, set the temperature to 1000 °C, and heat it.
2) Once the furnace temperature reaches 1000 °C, move the outer quartz tube into the furnace at a rate of 1 cm per 3 minutes[*368] to thermally decompose the sample. After the CB boat has completely entered the furnace, hold for 15 minutes[*369].
3) Move the outer tube within the tubular electric furnace toward its tip at a rate of 2 cm per 1.5 minutes while heating. After reaching the tip, hold for approximately 5 minutes[*370].
4) Turn off the furnace and remove the bubbler tube and snap tube from the outer tube.
5) Using paper wipes moistened with acetone and ethanol, wipe off the grease applied to the outer tube and the bubbler tube[*371].
6) Using a micropipette, wash the inside and outside of the bubbler tube with 0.14 mL of the TMAH solution, followed by washing with 4 mL of ultrapure water. Add the cleaning solution to the snap tube containing the iodine-absorbing solution.
7) Weigh the snap tube and calculate the weight of the iodine-absorbing solution.
8) The snap tube containing the iodine-absorbing solution should be sealed with fluoroplastic tape wrapped between the lid and the snap tube and stored in a light-shielded container covered with aluminum foil.

(4) Preparation of the iodine-absorbing solution for $^{127}I$ measurement

1) From the snap tube obtained in Step 8) of "(3) Thermal Hydrolysis," collect an aliquot and transfer it into a 100 mL volumetric flask[*372].
2) Add approximately 0.15 mL of the sodium hypochlorite solution and rinse any solution adhering to the inner wall of the volumetric flask with a small amount of ultrapure water. Allow standing for approximately 15 minutes.

[*367] When the ultrapure water in the water bath boils, switch off the water bath.
[*368] If the quartz outer tube is moved very quickly, the temperature inside the furnace may drop. Maintain the temperature in the furnace at 1000 °C at all times. In samples with a high organic content, incomplete combustion may cause tar to adhere to the bubbler side.
[*369] Ensure that vanadium pentoxide and the sample are in a completely molten state before proceeding to Step 3).
[*370] During Steps 1)–3), always check for oxygen gas bubbles released from the bubbler tube.
[*371] The outer tube and the bubbler tube may reach elevated temperatures during operation; direct contact shall be avoided to prevent burn injuries.
[*372] The dilution factor should be adjusted according to the amount of iodine present in the sample, and the measurement sample solution should be prepared according to the measurement conditions. (Typically, kombu (kelp) samples should be aliquoted at approximately 0.01 mL so that the concentration falls within the 0.0–10.0 ppb calibration range.)

3) Add a small amount of nitric acid (1 + 13) to the solution from Step 2), add an indium solution (1 $\mu$gIn/mL) as an internal standard, and then add nitric acid (1 + 13) up to the calibration mark of the volumetric flask. Shake well to prepare the measurement sample solution[*373].

### 4.2.3 Iodine Purification and Preparation of AMS Measurement Samples

(1) Separation and purification of iodine (solvent extraction)

1) To the remaining solution from Step 1) of "(4) Preparation of the iodine-absorbing solution for $^{127}$I measurement" in "4.2.2 Iodine Capture by Thermal Hydrolysis," add 1 mL of the iodine carrier solution (10 mg I/mL). Transfer the resulting solution to a 100 mL separatory funnel containing 20 mL of xylene.
2) Add ~3 mL of nitric acid and shake to adjust the pH level to 1.
3) Add 0.5 mL of the sodium nitrite solution (10 w/v%) and shake the separatory funnel vigorously for 1 minute while releasing gases[*374].
4) After leaving to stand, transfer the aqueous phase to a new 100 mL separatory funnel containing 20 mL of xylene[*375].
5) Add 20 mL of ultrapure water to the organic phase.
6) Shake the separatory funnel containing the aqueous phase of Step 4) vigorously for 1 minute. After leaving to stand, discard the aqueous phase and combine the organic phase with that from Step 5).
7) Add 1.0 mL of the sodium sulfite solution (10 w/v%) to the separatory funnel from Step 5). Shake the separatory funnel vigorously for 1 minute while releasing gases[*376].
8) Transfer the aqueous phase to a 50 mL beaker. Leave the organic phase in the separatory funnel, and add 20 mL of ultrapure water and 0.5 mL of the sodium sulfite solution (10 w/v%) to the funnel[*377].
9) Shake the separatory funnel vigorously for 1 minute while releasing gases.
10) Combine the aqueous phase with that from Step 8) and discard the organic phase.
11) Heat the combined solution from Step 10) on a hot plate to concentrate it to a volume of 10–20 mL. After cooling, transfer it to a 50 mL plastic centrifuge tube. This solution is used as the target preparation solution[*378].

(2) Preparation of the silver iodide precipitate

1) Add ultrapure water to the target preparation solution prepared in "(1) Separation and purification of iodine (solvent extraction)" so that the final volume is approximately

[*373] The internal-standard elements may be introduced using the online addition method described in "II. Triple Quadrupole ICP–MS."
[*374] Iodide ions ($I^-$) are oxidized to molecular iodine ($I^2$). (The organic phase changes from colorless to pink.)
[*375] In addition to xylene, benzene and toluene can be used; however, appropriate safety precautions must be taken.
[*376] Molecular iodine ($I^2$) is reduced to iodide ions ($I^-$). (The organic phase changes from pink to colorless.)
[*377] If the peach color does not disappear, add more sodium sulfite solution as needed.
[*378] The concentration should be adjusted as appropriate depending on the amount of iodide ions.

30 mL. Then, add 1 mL of ammonia water and 3–5 mL of the silver carrier solution (10 mg Ag/mL)[*379] to precipitate silver iodide (AgI).

2) After visually confirming the formation of the silver iodide precipitate in Step 1), wrap the plastic centrifuge tube with aluminum foil to shield it from light and then centrifuge the sample.
3) Remove the supernatant using a micropipette or similar tool, add ~30 mL of ultrapure water and 1 mL of the ammonia solution, shake vigorously, and then centrifuge.
4) Remove the supernatant using a micropipette, add 10 mL of ultrapure water, shake vigorously, and centrifuge.
5) Remove the supernatant using a micropipette, add 10 mL of ethanol, shake vigorously, and centrifuge.
6) Weigh the tare weight of the microtube.
7) After leaving to stand, remove ~2–3 mL of the supernatant from Step 5) using a micropipette. Mix the remaining silver iodide precipitate with ethanol and transfer it to the microtube.
8) Centrifuge the microtube containing the silver iodide precipitate, remove the supernatant, and dry under an infrared lamp until ethanol has completely evaporated.
9) Weigh the microtube and calculate the weight of the silver iodide precipitate.

(3) Preparation of the AMS target sample

Perform the same procedure as described in "(3) Preparation of the AMS measurement sample" in "1.2.3 Iodine Purification and Preparation of AMS Measurement Samples" of "Chapter 1 Airborne Particulate Matter Samples."

[*379] The amount of the silver carrier added should be three times the amount of iodine ions.

# Chapter 5 Vegetable

In this chapter, Chinese cabbage (*hakusai*) and cabbage are described as examples of analyzed vegetable samples.

Samples that have been freeze-dried in advance are used for analysis. The samples are subjected to thermal hydrolysis, and released iodine is collected using a strongly alkali solution. An aliquot of the resulting collection solution is used to measure $^{127}I$. After aliquoting, an iodine carrier solution is added to the remaining collection solution, and iodine is separated and purified using the solvent extraction method. A silver nitrate solution is then added to form a silver iodide precipitate, from which a target for AMS measurement is prepared.

The concentration of $^{129}I$ in the sample is determined from the atomic number ratio $^{129}I/^{127}I$ obtained by AMS measurement and the previously measured amount of $^{127}I$ in the sample.

## 5.1 Equipment, Instruments, and Reagents

(1) Equipment

1) Tubular electric furnace (equipped with a temperature controller and gas flowmeter; max temperature: ≥1000 °C; Figure III.1.2)
2) Electronic balance (minimum displayed value: 0.1 mg)
3) Ultrapure water production system
4) Centrifuge
5) Dryer
6) Ultrasonic cleaner
7) Freeze-dryer

(2) Instruments

1) Quartz tubes
   - Quartz outer tube (Figure III.1.2)
   - Quartz inner tube (Figure III.1.3)
2) Bubbler tube (Figure III.1.4)[*380]
3) Quartz wool
4) Clamp
5) Beakers (100 mL, 500 mL, and 5 L)
6) Watch glass (for a 100 mL beaker)
7) Volumetric flasks (25 mL, 50 mL, and 100 mL)
8) Separatory funnel (100 mL)
9) 50 mL plastic centrifuge tubes
10) 26 mL snap tubes
11) Water bath
12) Fluoroplastic tape

[*380] JIS standard G2, ISO standard P40 (pore size specification: 40–50 μm).

13) Spatulas and stainless steel spoons
14) Micro spatula
15) CB boat (or half-split quartz glass; 15 mm × 13 mm × 90 mm)
16) Agate mortar
17) Desiccator
18) 3 mL glass microtubes
19) Micropipettes (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
20) Pipette tips (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
21) Glass rod
22) Aluminum foil
23) Infrared lamp
24) Hot plate
25) Gas burner
26) Desiccator
27) Polypropylene containers

(3) Reagents

The mass and volume figures provided here are only examples of preparation ratios and may be adjusted as necessary during actual preparation. Reagents conforming to the JIS should be used. For nonstandard reagents, those with the highest possible purity should be used.

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*381,*382] in 100 mL of ultrapure water.
2) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of ultrapure water.
3) Nitric acid (1 + 13): Mix 1 part of nitric acid[*382,*383,*384] (mass fraction: 60%–61% (~13 mol/L); density: 1.38 g/mL; used for measuring toxic metals) with 13 parts of ultrapure water.
4) Low-level iodine carrier solution (5 mgI/mL)

[*381] Classified as Class 1 Hazardous Materials (Oxidizing Solids) under the Fire Service Act. Care should be taken to avoid contact with strong acids, storage with combustible materials, heating, impact, and friction.
[*382] Substances subject to the Poisonous and Deleterious Substances Control Act (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." Further, appropriate measures must be taken to prevent theft, loss, leakage, and similar incidents.
[*383] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures must be taken to reduce exposure concentrations, such as by installing local exhaust ventilation systems.
[*384] Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act (substances that may pose risks to workers or cause health impairment) must be clearly labeled, accompanied by safety data sheets, and assessed for risks (including the implementation of appropriate risk-reduction measures). Employers should ensure that workers are informed of and educated in the safe handling of such substances.

5) Silver nitrate solution (10 mgAg/mL): Weigh 1.575 g of silver nitrate[*382,*384], dissolve in ultrapure water, transfer the resulting solution to a 100 mL volumetric flask, and dilute up to the calibration mark with ultrapure water.
6) Xylene[*382,*384,*385,*386]
7) Acetone[*382,*384,*387]
8) Methanol[*382,*384,*387]
9) Ammonia water[*382,*383,*384] (mass fraction: 28.0%–30.0%)
10) TMAH solution[*382,*384,*387] (mass fraction: 25%)
11) Sodium hypochlorite (effective chlorine content of 4% or more; food additive grade)
12) Gases
    ・Oxygen gas (purity ≥ 99.999%)
    ・City gas or propane gas
13) Niobium powder[*382]
14) Vanadium pentoxide[*382,*384,*385]
15) Ultrapure water (purified to a resistivity of 18 MΩ·cm or higher[388])

## 5.2 Analytical Operations

### 5.2.1 Analysis and Sample Pretreatments

(1) Glassware

Perform the same operations as those described in "(1) Glassware" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(2) CB boat (or half-split quartz glass)

Perform the same procedure as those described in "(2) CB board (or half-split quartz glass)" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(3) Blank firing of the outer tube, inner tube, and CB boat

Perform the same operations as those described in "(3) Blank firing of the outer tube, inner tube, and CB boat" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

[*385] Category II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Category I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, are required.
[*386] This refers to the guidelines established by the Ministry of Health, Labour and Welfare pursuant to Article 28, Paragraph 3 of the Industrial Safety and Health Act for the prevention of health hazards caused by chemical substances. Measures should be taken to reduce exposure to target substances.
[*387] Classified as a Category IV Hazardous Material (Flammable Liquid) under the Fire Service Act. Use of open flames is strictly prohibited. Store and handle the material below the flash point. Keep away from Category I and Category V Hazardous Materials. Take precautions against static electricity generation. Avoid filling containers completely when repackaging to prevent rupture due to thermal expansion.
[*388] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

(4) Sample pretreatment

Perform the same operations as those described in "(4) Sample pretreatment" in "4.2.1 Analysis Preparation" of "Chapter 4 Seaweed."

### 5.2.2 Iodine Capture by Thermal Hydrolysis

(1) Preparation of the iodine-absorbing solution

1) Measure the weight of the empty 26 mL snap tube.
2) Using a micropipette, add the following to the snap tube in the given order: 8 mL of ultrapure water, 0.09 mL of the TMAH solution, 0.25 mL of the sodium sulfite solution (10 w/v%), and 8 mL of ultrapure water. This solution is used as the iodine-absorbing solution for $^{129}I$ measurement.

(2) Weighing of samples and preparation for combustion

1) Weigh ~2.0 g of vanadium pentoxide and place nearly one-third of it into the CB boat.
2) Weigh 2.0 g of the sample and place it on top of the CB boat[*389].
3) Cover the sample on the CB boat with the remaining vanadium pentoxide from Step 1), thus sandwiching the sample between layers of vanadium pentoxide.
4) Place this structure in the inner tube.
5) Apply grease to the sliding portion of the outer tube, connect the bubbler tube and the quartz outer tube, and fasten with a clamp.
6) Place the bubbler tube in the snap tube containing the iodine-absorbing solution prepared in "(1) Preparation of the iodine-absorbing solution" and cover with fluoroplastic tape.
7) Insert the assembly from Step 4) into the assembly prepared in Step 5).
8) Connect the inner and outer tubes to oxygen gas lines and adjust the oxygen flow rate to 10.0 mL/min for the inner tube and 12.5 mL/min for the outer tube.
9) Confirm that oxygen gas bubbles are released from the bubbler tube in Step 6). If no bubbles are observed, check all connections.

(3) Thermal hydrolysis

1) Switch on the water bath[*390]. Turn on the furnace, set the temperature to 1000 °C, and heat it.
2) Once the furnace temperature reaches 1000 °C, move the outer quartz tube into the furnace at a rate of 1 cm per 3 minutes[*391] to thermally decompose the sample. After the CB boat has completely entered the furnace, hold for 15 minutes[*392].

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[*389] When handling dried vegetable powder, care must be taken to avoid static electricity generation. (It is recommended to use a static eliminator. In some cases, after weighing and transferring the sample to the CB boat, it may be necessary to measure and subtract the weight of the remaining sample.)

[*390] When the ultrapure water in the water bath boils, switch off the water bath.

[*391] If the outer tube is moved very quickly, the temperature inside the tubular electric furnace may drop. Maintain the temperature in the electric furnace at 1000 °C at all times. In samples with a high organic content, incomplete combustion may cause tar to adhere to the bubbler side.

[*392] Ensure that vanadium pentoxide and the sample are in a completely molten state before proceeding to Step 3). In addition, vegetables and other samples are prone to clogging due to the tar produced during thermal decomposition.

3) Move the outer tube from inside the furnace toward its tip at a rate of 2 cm per 1.5 min and heat it. After reaching the tip, hold for approximately 5 minutes[*393].
4) Turn off the furnace and remove the bubbler tube and snap tube from the outer tube.
5) Using paper wipes moistened with acetone and ethanol, wipe off the grease applied to the outer tube and the bubbler tube[*394].
6) Using a micropipette, wash the inside and outside of the bubbler tube with 0.05 mL of the TMAH solution and 4 mL of ultrapure water in that order. Add the cleaning solution to the snap tube containing the iodine-absorbing solution.
7) Weigh the snap tube and calculate the weight of the iodine-absorbing solution.
8) The snap tube containing the iodine-absorbing solution should be sealed with fluoroplastic tape wrapped between the lid and the snap tube and stored in a light-shielded container covered with aluminum foil.

(4) Preparation of the iodine-absorbing solution for $^{127}$I measurement

1) From the snap tube obtained in Step 8) of "(3) Thermal Hydrolysis," collect an aliquot and transfer it into a 100 mL volumetric flask[*395].
2) Add approximately 0.15 mL of the sodium hypochlorite solution and rinse any solution adhering to the inner wall of the volumetric flask with a small amount of ultrapure water. Allow standing for approximately 15 minutes.
3) Add a small amount of nitric acid (1 + 13) to the solution from Step 2), add an indium solution (1 $\mu$gIn/mL) as an internal standard, and then add nitric acid (1 + 13) up to the calibration mark of the volumetric flask. Shake well to prepare the measurement sample solution[*396].

### 5.2.3 Iodine Purification and Preparation of AMS Measurement Samples

(1) Separation and purification of iodine (solvent extraction)

1) To the remaining solution after Step 1) of "(4) Preparation of the iodine-absorbing solution for $^{127}$I measurement" in "5.2.2 Iodine Capture by Thermal Hydrolysis," add 0.6 mL of the low-level iodine carrier (5 mg I/mL) and transfer the mixture into a 100-mL separatory funnel containing 20 mL of xylene.
2) Add ~3 mL of nitric acid and shake to adjust the pH level to 1.
3) Add 0.5 mL of the sodium nitrite solution (10 w/v%) and shake the separatory funnel vigorously for 1 minute while releasing gases[*397].

[*393] During Steps 1)–3), always check for oxygen gas bubbles released from the bubbler tube.
[*394] The outer tube and the bubbler tube may reach elevated temperatures during operation; direct contact shall be avoided to prevent burn injuries.
[*395] The dilution factor should be adjusted according to the amount of iodine present in the sample, and the measurement sample solution should be prepared according to the measurement conditions. (Typically, for Chinese cabbage or cabbage, the sample should be aliquoted at approximately 2 mL so that the concentration falls within the 0.0–10.0 ppb calibration range.)
[*396] The internal-standard elements may be introduced using the online addition method described in "II. Triple Quadrupole ICP–MS."
[*397] Iodide ions ($I^-$) are oxidized into molecular iodine ($I_2$). (The organic phase changes color from colorless to pink.)

4) After leaving to stand, transfer the aqueous phase to a new 100 mL separatory funnel containing 20 mL of xylene[*398].
5) Add 20 mL of ultrapure water to the organic phase.
6) Shake the separatory funnel containing the aqueous phase of Step 4) vigorously for 1 minute. After leaving to stand, discard the aqueous phase and combine the organic phase with that from Step 5).
7) Add 0.5 mL of the sodium sulfite solution (10 w/v%) to the separatory funnel from Step 5). While releasing gases, shake the separatory funnel vigorously for 1 minute[*399].
8) Transfer the aqueous phase to a 50 mL beaker. Leave the organic phase in the separatory funnel, and add 20 mL of ultrapure water and 0.1 mL of the sodium sulfite solution (10 w/v%) to the funnel[*400].
9) Shake the separatory funnel vigorously for 1 minute while releasing gases.
10) Combine the aqueous phase with that from Step 8) and discard the organic phase.
11) Concentrate the combined solution from Step 10) on a hot plate by heating until the volume is reduced to 5 mL. After cooling, transfer it to a 50 mL plastic centrifuge tube. This is the target preparation solution[*401].

(2) Preparation of the silver iodide precipitate

1) Add ultrapure water to the target preparation solution prepared in "(1) Separation and purification of iodine (solvent extraction)" so that the final volume is approximately 10 mL. Then, add 0.5 mL of ammonia water and 1.5–2.5 mL of the silver carrier solution (10 mg Ag/mL)[*402] to precipitate silver iodide (AgI).
2) After visually confirming the formation of the silver iodide precipitate in Step 1), wrap the plastic centrifuge tube with aluminum foil to shield it from light and then centrifuge.
3) Remove the supernatant using a micropipette. Add approximately 10 mL of ultrapure water and 0.5 mL of ammonia water, shake vigorously, and then centrifuge.
4) Remove the supernatant using a micropipette, add 10 mL of ultrapure water, shake vigorously, and centrifuge.
5) Remove the supernatant using a micropipette, add 10 mL of ethanol, shake vigorously, and centrifuge.
6) Weigh the tare weight of the microtube.
7) After leaving to stand, remove ~2–3 mL of the supernatant using a micropipette. Mix the remaining silver iodide precipitate with ethanol and transfer it to the microtube.
8) Centrifuge the microtube containing the silver iodide precipitate, remove the supernatant, and dry under an infrared lamp until ethanol has completely evaporated.

[*398] In addition to xylene, benzene and toluene can be used; however, appropriate safety precautions must be taken.
[*399] Molecular iodine ($I_2$) is reduced into iodide ions ($I^-$). (The organic phase changes color from pink to colorless.)
[*400] If the peach color does not disappear, add more sodium sulfite solution as needed.
[*401] The concentration should be adjusted as appropriate depending on the amount of iodide ions.
[*402] The amount of the silver carrier added should be three times the amount of iodine ions.

9) Weigh the microtube and calculate the weight of the silver iodide precipitate.

(3) Preparation of the AMS target sample

Perform the same procedure as described in "(3) Preparation of the AMS measurement sample" in "1.2.3 Iodine Purification and Preparation of AMS Measurement Samples" of "Chapter 1 Airborne Particulate Matter Samples."

# Chapter 6 Milk

When analyzing milk, samples that have been freeze-dried in advance are used. The samples are subjected to thermal hydrolysis, and released iodine is collected using a strongly alkali solution. An aliquot of the resulting collection solution is used for $^{127}I$ measurement. After aliquoting, an iodine carrier solution is added to the remaining collection solution, and iodine is separated and purified using the solvent extraction method. A silver nitrate solution is then added to form a silver iodide precipitate, from which a target for AMS measurement is prepared.

The $^{129}I$ concentration in the sample is determined from the $^{129}I/^{127}I$ atomic ratio obtained by AMS measurement and the previously measured amount of $^{127}I$ in the sample.

## 6.1 Equipment, Instruments, and Reagents

(1) Equipment

1) Tubular electric furnace (equipped with a temperature controller and gas flowmeter; max temperature ≥1000 °C; Figure III.1.2)
2) Electronic balance (minimum displayed value: 0.1 mg)
3) Ultrapure water production system
4) Centrifuge
5) Dryer
6) Ultrasonic cleaner

(2) Instruments

1) Quartz tubes
   - Quartz outer tube (Figure III.1.2)
   - Quartz inner tube (Figure III.1.3)
2) Bubbler tube (Figure III.1.4)[*403]
3) Quartz wool
4) Clamp
5) Beakers (100 mL, 500 mL, and 5 L)
6) Watch glass (for 100 mL beakers)
7) Volumetric flasks (25 mL, 50 mL, and 100 mL)
8) Separatory funnel (100 mL)
9) 50 mL plastic centrifuge tubes
10) 26 mL snap tubes
11) Water bath
12) Fluoroplastic tape
13) Spatulas and stainless steel spoons
14) Micro spatula

[*403] JIS standard G2, ISO standard P40 (pore size specification: 40–50 μm).

15) CB boat (or half-split quartz glass; 15 mm × 13 mm × 90 mm)
16) Agate mortar
17) Desiccator
18) 3 mL glass microtubes
19) Micropipettes (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
20) Pipette tips (0.1 mL, 1 mL, 2 mL, 5 mL, and 10 mL)
21) Glass rod
22) Aluminum foil
23) Infrared lamp
24) Hot plate
25) Gas burner
26) Desiccator
27) Polypropylene containers

(3) Reagents

The mass and volume figures provided here are only examples of preparation ratios and may be adjusted as necessary during actual preparation. Reagents conforming to the JIS should be used. For non-standard reagents, those with the highest possible purity should be used.

1) Sodium nitrite solution (10 w/v%): Dissolve 10 g of sodium nitrite[*404,*405] in 100 mL of ultrapure water.
2) Sodium sulfite solution (10 w/v%): Dissolve 10 g of sodium sulfite in 100 mL of ultrapure water.
3) Nitric acid (1 + 13): Mix 1 part of nitric acid[* 405 ,* 406 ,* 407] (mass fraction: 60%–61% (~13 mol/L); density: 1.38 g/mL; used for measuring toxic metals) with 13 parts of ultrapure water.
4) Low-level iodine carrier solution (5 mgI/mL)
5) Silver nitrate solution (10 mgAg/mL): Weigh 1.575 g of silver nitrate[*405,*407], dissolve in ultrapure water, transfer to a 100 mL volumetric flask, and dilute up to the calibration mark with ultrapure water.

[*404] Classified as Class 1 Hazardous Materials (Oxidizing Solids) under the Fire Service Act. Care should be taken to avoid contact with strong acids, storage with combustible materials, heating, impact, and friction.

[*405] Substances subject to the Poisonous and Deleterious Substances Control Act (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." Further, appropriate measures must be taken to prevent theft, loss, leakage, and similar incidents.

[*406] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures must be taken to reduce exposure concentrations, such as by installing local exhaust ventilation systems.

[*407] Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act (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 should ensure that workers are informed of and educated in the safe handling of such substances.

6) Xylene[*405,*407,*408,*409]
7) Acetone[*405,*407,*410]
8) Methanol[*405,*407,*410]
9) Ammonia water[*405,*406,*407] (mass fraction: 28%–30%)
10) TMAH solution[*405,* 407,*410] (mass fraction: 25%)
11) Sodium hypochlorite (effective chlorine content of 4% or more; food additive grade)
12) Gases
- Oxygen gas (purity ≥ 99.999%)
- City gas or propane gas

13) Niobium powder[*405]
14) Vanadium pentoxide[*405,*407,*408]
15) Ultrapure water (purified to a resistivity of 18 MΩ·cm or higher[*411])

## 6.2 Analytical Operations

### 6.2.1 Analysis and Sample Pretreatments

(1) Glassware

Perform the same operations as those described in "(1) Glassware" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(2) CB boat (or half-split quartz glass)

Perform the same operations as those described in "(2) CB board (or half-split quartz glass)" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter Samples."

(3) Blank firing of the outer tube, inner tube, and CB boat

Perform the same operations as those described in "(3) Blank firing of the outer tube, inner tube, and CB boat" in "1.2.1 Analysis and Sample Pretreatments" of "Chapter 1 Airborne Particulate Matter."

(4) Sample pretreatment

Perform the same operations as those described in "(4) Sample pretreatment" in "4.2.1 Analysis Preparation" in "Chapter 4 Seaweed."

### 6.2.2 Iodine Capture by Thermal Hydrolysis

[*408] Category II Substances under the Ordinance on the Prevention of the Hazard due to Specified Chemical Substances (substances that cause chronic disorders such as cancer but do not fall under Category I substances): Measures to reduce exposure concentrations, such as installing local exhaust ventilation systems, are necessary.

[*409] This refers to the guidelines established by the Ministry of Health, Labour and Welfare, pursuant to Article 28, Paragraph 3 of the Industrial Safety and Health Act, for the prevention of health hazards caused by chemical substances. Measures should be undertaken to reduce exposure to target substances.

[*410] Classified as a Class IV Hazardous Material (flammable liquids) under the Fire Service Act. Following precautions are necessary: Open flames must be strictly avoided. Store and handle the material below its flash point. Ensure separate storage from Category I and Category V Hazardous Substances. Implement measures to avoid static electricity generation. When transferring to smaller containers, avoid filling to full capacity to prevent potential rupture due to thermal expansion.

[*411] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

(1) Preparation of the iodine-absorbing solution

1) Weigh the empty snap tube.
2) Using a micropipette, add the following to the snap tube in the given order: 8 mL of ultrapure water, 0.09 mL of the TMAH solution, 0.25 mL of the sodium sulfite solution (10 w/v%), and 8 mL of ultrapure water. This solution is used as the iodine-absorbing solution for $^{129}I$ measurement.

(2) Weighing of samples and preparation for combustion

1) Weigh approximately 2.0 g of vanadium pentoxide and place about one-third of it in the CB boat.
2) Weigh 1.5 g of the sample and place it on top of the CB boat.
3) Cover the sample on the CB boat with the remaining vanadium pentoxide from Step 1), thus sandwiching the sample between layers of vanadium pentoxide.
4) Place the assembly from Step 3) in the quartz inner tube.
5) Apply grease to the sliding portion of the quartz outer tube, connect the bubbler tube and the quartz outer tube, and fasten with a clamp.
6) Place the bubbler tube in the snap tube containing the iodine-absorbing solution prepared in "(1) Preparation of the iodine-absorbing solution" and cover with fluoroplastic tape.
7) Insert the assembly from Step 4) into the assembly prepared in Step 5).
8) Connect the quartz inner and outer tubes to oxygen gas lines and adjust the oxygen flow rate to 10.0 mL/min for the inner tube and 11.0 mL/min for the outer tube.
9) Confirm that bubbles are released from the bubbler tube in Step 6). If bubbles do not appear, check the connection points.

(3) Thermal hydrolysis

1) Switch on the water bath[*412]. Turn on the tubular-type electric furnace, set the temperature to 1000 °C, and heat it.
2) Once the furnace temperature reaches 1000 °C, move the outer quartz tube into the furnace at a rate of 1 cm per 3 minutes[*413] to thermally decompose the sample. After the CB boat has completely entered the furnace, hold for 20 minutes[*414].
3) Move the outer tube from inside the furnace toward its tip at a rate of 2 cm per 1.5 min and heat it. After reaching the tip, hold for approximately 5 minutes[*415].
4) Turn off the furnace and remove the bubbler tube and snap tube from the outer tube.
5) Using paper wipes moistened with acetone and ethanol, wipe off the grease applied to the

[*412] When the ultrapure water in the water bath boils, switch off the water bath.
[*413] If the outer tube is moved very quickly, the temperature inside the tubular electric furnace may drop. Maintain the temperature in the electric furnace at 1000 °C at all times. In samples with a high organic content, incomplete combustion may cause tar to adhere to the bubbler side.
[*414] Ensure that vanadium pentoxide and the sample are in a completely molten state before proceeding to Step 3). Vegetables and other samples a prone to clogging due to the tar produced during thermal decomposition.
[*415] Always check for air bubbles released from the bubbler tube during Steps 1)–3).

outer tube and the bubbler tube[*416].

6) Using a micropipette, wash the inside and outside of the bubbler tube with 0.05 mL of the TMAH solution and 4 mL of ultrapure water in that order. Add the cleaning solution to the snap tube containing the iodine-absorbing solution.
7) Weigh the snap tube and calculate the weight of the iodine-absorbing solution.
8) The snap tube containing the iodine-absorbing solution should be sealed with fluoroplastic tape wrapped between the lid and the snap tube and stored in a light-shielded container covered with aluminum foil.

(4) Preparation of the iodine-absorbing solution for $^{127}$I measurement

1) From the snap tube obtained in Step 8) of "(3) Thermal Hydrolysis," collect an aliquot and transfer it into a 100 mL volumetric flask[*417].
2) Add approximately 0.15 mL of the sodium hypochlorite solution and rinse any solution adhering to the inner wall of the volumetric flask with a small amount of ultrapure water. Allow to stand for approximately 15 minutes.
3) Add a small amount of nitric acid (1 + 13) to the solution from Step 2), add indium solution (1 $\mu$gIn/mL) as an internal standard, and then dilute to the calibration mark with nitric acid (1 + 13). Shake well to prepare the measurement sample solution[*418].

### 6.2.3 Iodine Purification and Preparation of AMS Measurement Samples

(1) Separation and purification of iodine (solvent extraction)

1) Add 0.6 mL of the low-level iodine carrier solution (5 mg I/mL) to the solution remaining after Step 1) of "(4) Preparation of the iodine-absorbing solution for $^{127}$I measurement" in "6.2.2 Iodine Capture by Thermal Hydrolysis."

   Then, transfer the mixture to a 100 mL separatory funnel containing 20 mL of xylene.
2) Add ~3 mL of nitric acid and shake to adjust the pH level to 1.
3) Add 0.5 mL of the sodium nitrite solution (10 w/v%) and shake the separatory funnel vigorously for 1 minute while releasing gases[*419].
4) After leaving to stand, transfer the aqueous phase to a new 100 mL separatory funnel containing 20 mL of xylene[*420].
5) Add 20 mL of ultrapure water to the organic phase.
6) Shake the separatory funnel containing the aqueous phase of Step 4) vigorously for 1 minute. After leaving to stand, discard the aqueous phase and combine the organic phase with that from Step 5).

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[*416] The outer tube and the bubbler tube may reach elevated temperatures during operation; direct contact shall be avoided to prevent burn injuries.
[*417] The dilution factor should be adjusted according to the amount of iodine present in the sample, and the measurement sample solution should be prepared according to the measurement conditions. (Typically, for Chinese cabbage or cabbage, the sample should be aliquoted at approximately 2 mL so that the concentration falls within the 0.0–10.0 ppb calibration range.)
[*418] The internal-standard elements may be introduced using the online addition method described in "II. Triple Quadrupole ICP–MS."
[*419] Iodide ions (I−) are oxidized into molecular iodine (I2). (The organic phase changes color from colorless to pink.)
[*420] In addition to xylene, benzene and toluene can be used; however, appropriate safety precautions must be taken.

7) Add 0.1 mL of the sodium sulfite solution (10 w/v%) to the separatory funnel from Step 5). Shake the separatory funnel vigorously for 1 minute while releasing gases[*421].

8) Transfer the aqueous phase to a 50 mL beaker. Leave the organic phase in the separatory funnel, and add 20 mL of ultrapure water and 0.1 mL of the sodium sulfite solution (10 w/v%)[*422] to the funnel.

9) Shake the separatory funnel vigorously for 1 minute while releasing gases.

10) Combine the aqueous phase with that from Step 8) and discard the organic phase.

11) Heat the combined solution from Step 10) on a hot plate to concentrate it to a final volume of 10–20 mL. After cooling, transfer it to a 50 mL plastic centrifuge tube. This solution is used as the target preparation solution[*423].

(2) Preparation of the silver iodide precipitate

1) Add ultrapure water to the target preparation solution prepared in "(1) Separation and purification of iodine (solvent extraction)" so that the final volume is approximately 10 mL. Then, add 0.5 mL of ammonia water and 3–5 mL of the silver carrier solution (1 mgAg/mL)[*424] to precipitate silver iodide (AgI).

2) After visually confirming the formation of the silver iodide precipitate in Step 1), wrap the plastic centrifuge tube with aluminum foil to shield it from light and then centrifuge.

3) Remove the supernatant using a micropipette. Add approximately 10 mL of ultrapure water and 0.5 mL of ammonia water, shake vigorously, and then centrifuge.

4) Remove the supernatant using a micropipette, add 10 mL of ultrapure water, shake vigorously, and centrifuge.

5) Remove the supernatant using a micropipette, add 10 mL of ethanol, shake vigorously, and centrifuge.

6) Weigh the tare weight of the microtube.

7) After leaving to stand, remove ~2–3 mL of the supernatant from Step 5) using a micropipette. Mix the remaining silver iodide precipitate with ethanol and transfer it to the microtube.

8) Centrifuge the microtube containing the silver iodide precipitate, remove the supernatant, and dry under an infrared lamp until ethanol has completely evaporated.

9) Weigh the microtube and calculate the net weight of the silver iodide precipitate.

(3) Preparation of the AMS target sample

Perform the same procedure as described in "(3) Preparation of the AMS measurement sample" in "1.2.3 Iodine Purification and Preparation of AMS Measurement Samples" of "Chapter 1 Airborne Particulate Matter Samples."

[*421] Molecular iodine ($I_2$) is reduced to iodide ions ($I^-$). (The organic phase changes color from pink to colorless.)
[*422] If the peach color does not disappear, add more sodium sulfite solution as needed.
[*423] The concentration should be adjusted as appropriate depending on the amount of iodide ions.
[*424] The amount of the silver carrier added should be three times the amount of iodine ions.

# Chapter 7 Measurement

## 7.1 Determination of $^{127}I$ by ICP–MS

An ICP–MS device consists of a sample introduction system, an ionization section (ICP chamber), an interface section, an ion lens system, a mass separation section (radio-frequency quadrupole or magnetic field sector), a detector, a system control unit, and a data output unit. The ICP in the ionization section is a donut-shaped plasma with a high temperature (6000–10,000 K) and high electron density ($10^{15}$ $cm^{-3}$). Therefore, samples introduced via the nebulizer in the sample introduction system are efficiently ionized. The generated ions pass through the interface section, which consists of a sampling cone and a skimmer cone, are focused by the ion lens system, and are subsequently introduced into the mass separation section. In the mass separation section, ions with a specific mass-to-charge ratio (mass number/charge number or *m/z*) are selected and transmitted to the detector, where they are converted into readable signals and output as data.

For $^{127}I$ measurement, ions with a mass-to-charge ratio (*m/z*) of 127[*425] are measured. After chemical separation of iodine according to Chapters 1–6, the measurement samples prepared as nitric acid solutions are analyzed by ICP–MS. Determination is performed using the internal-standard method with indium. In this method, a known amount of indium is added to the measurement sample, and $^{127}I$ is quantified from the intensity ratio of signals at m/z 127 (iodine) and *m/z* 115 (indium).

### 7.1.1 Equipment, Instruments, and Reagents

(1) Equipment

1) Electronic balance (minimum displayed value: 0.0001 g)
2) Ultrapure water production system
3) ICP–MS device[*426]
4) Ultrasonic cleaner

(2) Instruments

1) Beakers (50 mL and 100 mL)
2) Micropipettes (0.1 mL, 1 mL, 2 mL, and 5 mL)
3) Pipette tips (0.1 mL, 1 mL, 2 mL, and 5 mL)
4) Glass rod
5) Plastic container (18 mL)

[*425] Under standard conditions and with standard equipment, the target of measurement is +1 valence state ($I^+$).
[*426] Addition of the internal standard described here is using the individual (offline) addition method rather than the online addition method.

(3) Reagents

The mass and volume figures provided here are only examples of preparation ratios and may be adjusted as necessary during actual preparation. Reagents conforming to the JIS should be used. For nonstandard reagents, those with the highest possible purity should be used.

1) $^{127}$I solution (10 mgI/mL): Dry ~3 g of potassium iodide at 110 °C for 3 hours and cool in a desiccator for 1 hour. Dissolve 1.309 g of potassium iodide in ultrapure water, add 2.3 g of sodium sulfite, transfer the resulting solution to a 100 mL volumetric flask, and dilute up to the calibration mark with ultrapure water.

2) Indium standard solution[*427,*428] (1 $\mu$gIn/mL): Dilute a commercially available solution (1,000 µgIn/mL) 1,000-fold with nitric acid (1 + 13).

3) Nitric acid (1 + 13): Mix 1 part of nitric acid[*427,*428,*429] (mass fraction: 60%–61% (~13 mol/L); density: 1.38 g/mL; used for measuring toxic metals) with 13 parts of ultrapure water.

4) Sodium hypochlorite (effective chlorine content of 4% or more; food additive grade)

5) $^{127}$I standard solution (0.1–10 $\mu$gI/L): Using a micropipette, accurately aliquot the $^{127}$I stock solution (10 mg I/mL) to prepare standard solutions with concentrations of 0.1, 0.5, 1.0, 5.0, and 10 $\mu$gI/L in different 100 mL volumetric flasks. Add 0.15 mL of the sodium hypochlorite solution and rinse the inner wall of the volumetric flasks with a small amount of ultrapure water. After 15 minutes, add a small amount of nitric acid (1 + 13), add 0.4 mL of the indium standard solution (1 $\mu$gIn/mL), and then add nitric acid (1 + 13) up to the calibration mark of the measuring flasks. Shake thoroughly and use these as the standard solutions for generating the calibration curve.

6) Gases

Helium gas (purity ≥ 99.999%)

Argon gas (purity ≥ 99.99%)

7) Ultrapure water (purified to a resistivity of 18 MΩ·cm or higher[*430])

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[*427] Class III Substances under the Ordinance on Prevention of Hazards Due to Specified Chemical Substances (substances that cause acute poisoning in the event of a large-scale leak): Measures must be undertaken to reduce exposure concentrations, such as by installing local exhaust ventilation systems.

[*428] Hazardous substances subject to labeling requirements under the Industrial Safety and Health Act (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 should ensure that workers are informed of and educated in the safe handling of such substances.

[*429] Substances subject to the Poisonous and Deleterious Substances Control Act (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.” Further, appropriate measures must be undertaken to prevent theft, loss, leakage, and similar incidents.

[*430] Defined in JIS K 0211: 分析化学用語(基礎部門) (2013), definition no. 5218.

### 7.1.2 Premeasurement Checks

Perform the following checks before igniting the plasma. For detailed information and procedures, refer to the equipment manufacturer's instructions.

(1) Check the sampling cone and skimmer cone for contamination[*431].

(2) Check the amount of cooling water[*432] in the cooling water circulation system.

(3) While introducing a solution, check for deterioration[*433] of the tubing associated with the ICP–MS device.

(4) Check the remaining amount[*434] of argon gas.

(5) Check the operation of the ICP–MS exhaust system.

### 7.1.3 Premeasurement Operations

Prior to sample measurement, perform the following operations.

(1) Instrument start-up

1) Open the argon gas valve.
2) Ignite on the plasma and confirm its stability.
3) Wait for ~30 minutes for the plasma to stabilize.

(2) Optimization of measurement conditions

1) Introduce nitric acid (1 + 13) and check the sample flow to the torch.
2) Using a tuning solution[*435], adjust sensitivity and perform mass-axis calibration[*436].
3) Introduce nitric acid (1 + 13), rinse the sample path to the torch, and check for changes in the *m/z* 127 counting rate.
4) Set the m/z values to be measured, measurement time, number of repeat measurements, sample pathway cleaning time, and other relevant conditions.[*437].
5) Set the measurement sequence for analytical, blank, and check samples, and then perform measurements.

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[*431] Since contamination of the cones reduces sensitivity and makes it difficult to obtain stable data, clean the cones according to the manufacturer's specific procedures.

[*432] If the cooling water is insufficient due to evaporation or other reasons, the ICP–MS device may not be adequately cooled, and the instrument may stop during measurement.

[*433] Deterioration of tubing due to repeated use can cause gas leaks and pulsations.

[*434] A single 7-$m^3$ cylinder can operate for ~4.5 hours. (This duration varies slightly depending on the conditions of use.) Meanwhile, portable liquefied gas systems contain 120-$m^3$ of argon gas in a 176-L cryogenic container (for liquid filling).

[*435] Normally, a standard solution of yttrium or thallium (approximately 10 ng/mL) is used.

[*436] This adjustment determines the sensitivity (lower detection limit, etc.).

[*437] The measurement time should be 3 seconds, and the number of repetitions should be 5 times for each measurement.

### 7.1.4 Determination of $^{127}$I

Perform the following steps to quantify $^{127}$I by measuring the prepared measurement solution.

(1) Determination procedure for $^{127}$I

1) Sequentially introduce calibration solutions prepared from the $^{127}$I standard solution (0.1–10 $\mu$gI/L), determine the intensity ratio of signals at *m/z* 127 and 115, and construct a calibration curve relating the $^{127}$I concentration to the intensity ratio.

2) Introduce the measurement sample solution. Then, from the intensity ratio of signals at *m/z* 127 and 115 and the calibration curve, determine the $^{127}$I concentration (ng/mL) in the measurement sample solution[*438].

(2) Calculation of the $^{127}$I concentration in the sample

Based on the obtained results, calculate the $^{127}$I concentration in the sample according to the following equations:

$$C = \frac{C_{127}}{P/W_s}$$

$$C_{127} = \frac{C_{S_{127}} \times w_{S_{127}} \times D_{S_{127}}}{10^6}$$

$C$ : $^{127}$I concentration in the sample (mg/kg, mg/L, etc.)

$C_{127}$ : Amount of $^{127}$I in the original measurement solution (mg)

$P$ : Aliquot fraction[*439]

$Ws$ : Sample amount (kg, L, etc.)

$C_{S127}$ : $^{127}$I concentration (ng/mL) in the measurement solution

$w_{S127}$ : Volume of the original $^{127}$I measurement solution (mL)[*440]

$D_{S127}$ : Dilution factor used when preparing the final $^{127}$I measurement solution from the original $^{127}$I measurement solution.[*441]

## 7.2 Determination of $^{129}$I by AMS

AMS is an analytical technique in which target ions are accelerated by an accelerator to high energies (on the order of megaelectron volts per nucleon) and then subjected to mass analysis. The high kinetic energy obtained by the accelerator can be used to eliminate isobaric and isobaric molecular ions that would substantially interfere with the detection of the target nuclide in ordinary mass spectrometry systems (with energies on the order of kiloelectron volts or so). This makes AMS an extremely high-sensitivity nuclide analysis technique.

An AMS system basically consists of ① an ion source, ② a low-energy analysis system, ③ an accelerator, (4) a high-energy analysis system (including a stable isotope measurement system), and ④ a detector (for detecting target nuclides). Most AMS systems currently in operation around

[*438] After measurement, introduce nitric acid (1 + 13) for at least 5 minutes to rinse the pathway. Before measuring the next sample, measure a blank sample to confirm that the background level has been reached.

[*439] In this method, the fraction is 0.01. Meanwhile, if no aliquot is taken, use a value of 1.

[*440] In this method, the measurement sample volume is 50 or 100 mL. When no dilution is performed, this should be interpreted as the $^{127}$I measurement solution.

[*441] Adjustment may be necessary depending on the $^{127}$I concentration. If no dilution is performed, this value is 1.

the world employ a tandem electrostatic accelerator (also called a tandem accelerator). In a tandem accelerator, the entrance and exit are at the ground potential, and a high potential is applied to the central electrode (called the terminal). Hence, particles to be accelerated must be injected as negative ions. Therefore, the system is combined with a negative ion source. For AMS, Cs sputter-type solid ion sources are most commonly used as negative ion sources, although gas ion sources may also be employed in some cases.

The solid material sputtered to generate negative ions (in the case of AMS, an individual measurement sample) is called the target. In AMS, converting the measurement sample into a form suitable for loading into the ion source is called "target preparation" or "target making." Since negative ions obtained from the target contain a large amount of ions other than the elements of the target nuclide, mass analysis is performed in the low-energy analysis system to select the ions to be injected into the accelerator. Negative ions entering the accelerator are accelerated from the entrance toward the terminal. The terminal contains a charge converter, which converts the negative ions into positive ions. Positive ions are then accelerated from the high potential of the terminal toward the ground potential of the output[*442]. After acceleration, the ions have various charge numbers and energies. The high-energy analysis electromagnet then selects ions with a specific charge number and energy from the accelerated ions.

In the AMS analysis of $^{129}$I (hereafter referred to as "$^{129}$I AMS"), the isotopic ratio of $^{129}$I (the target nuclide; present in trace amounts) to $^{127}$I (a stable isotope; present in abundance) of the target can be measured. In the low-energy analysis system, the magnetic field of the injection magnet is set so that ions with a mass number of 129 are selected and injected into the accelerator. However, at the time of injection into the magnet, the ions can be slightly accelerated, allowing ions with a mass number of 127 to be injected into the accelerator for a short period. By periodically applying this small accelerating voltage, ions with mass numbers of 129 and 127 are injected into the accelerator alternately. This method is called "sequential injection."

In $^{129}$I–AMS, an accelerating voltage of 3–5 MV is typically used in tandem accelerators and a charge state of 5+ is often selected on the high-energy side. The analyzing electromagnet is set to a magnetic field corresponding to $^{129}I^{5+}$. Since $^{127}I^{5+}$ ions accelerated by sequential injection follow a different orbit within the analyzing electromagnet, $^{127}I^{5+}$ can be measured by placing a Faraday cup at a position offset from the central orbit. Meanwhile, $^{129}I^{5+}$ ions are transported to the final detector, which is typically a gas ionization chamber.

In the gas ionization chamber, the number of incident $^{129}I^{5+}$ ions is counted, and the typical counting rate is on the order of 0.1–100 cps. Meanwhile, $^{127}I^{5+}$ is measured as an electric current using a Faraday cup, with typical values ranging from several hundred nanoamperes to several microamperes. The resulting isotopic ratio ($^{129}$I/$^{127}$I) is from $10^{-14}$ to $10^{-10}$. Because the abundances of the isotopes differ greatly and the detection methods are completely different, the measured results cannot be directly regarded as the intrinsic isotopic ratio of the target. It is therefore necessary to measure standard samples with known isotopic ratios and normalize the results using those measurements.

[*442] Because acceleration is performed in two stages, the system is called a tandem accelerator.

### 7.2.1 Equipment, Instruments, and Reagents

(1) Equipment

1) AMS device[*443]

(2) Instruments

1) Target piece (cathode): The powder sample prepared in Section 2.2.3 (3), or equivalent, is pressed into a target piece to serve as the ion source target. It is also called a cathode because the target itself functions as the negative electrode in the ion source. Several dozen cathodes are mounted together on a target wheel, which is then installed in the ion source and evacuated. Unknown samples, standard samples, and—if necessary—beam adjustment and blank samples are set on the same target wheel. After pressing, the time until the target wheel is installed in the ion source and evacuation begins should be kept as short as possible.

### 7.2.2 Precautions Regarding Measurement Instruments

(1) The ion source must be cleaned periodically. Conducting AMS measurements involves sputtering a large number of samples. Materials that are not ionized during sputtering gradually deposit on various parts of the chamber inside the ion source. If such contamination becomes significant, there is a risk of contaminating the measurement samples.

(2) An appropriate level of vacuum should be maintained. The space through which ions travel from the ion source to the final detector (inside the beam duct) is a vacuum. The vacuum should be at least equivalent to that achievable with a turbopump.

(3) Accelerator stability should be maintained. Fluctuations in the accelerator cause variations in ion energy, which ultimately reduce the transmission efficiency and affect the measurement accuracy. Daily maintenance is crucial to ensure accelerator stability.

To prevent electrical discharge at high voltage, it is important to monitor the dew point of the insulating gas ($SF_6$), which indicates the moisture content in the gas.

### 7.2.3 Premeasurement Operations

Prior to sample measurement, perform the following operations.

(1) Instrument start-up

1) Set the target wheel in the ion source and evacuate the system.

2) Set appropriate parameters for accelerators, analytical instruments (electrostatic deflectors and magnets), lenses (Einzel lens, electrostatic Q-lens, and magnetic Q-lens), stirrers, the

[*443] Accelerators capable of $^{129}I$ AMS include those manufactured by National Electrostatics Corporation (NEC; USA), High Voltage Engineering Europa (HVEE; Netherlands), and Ionplus (Switzerland). In Japan, NEC and HVEE systems are in use. As of 2023, domestic facilities capable of $^{129}I$ AMS include the Japan Atomic Energy Agency Aomori Research and Development Center, Japan Atomic Energy Agency Tono Geoscience Center, University of Tokyo Tandem Accelerator Research Facility, University of Tsukuba Center for Research in Isotopes and Environmental Dynamics, and National Institute for Environmental Studies.

sequential injection system, Faraday cups for stable isotope measurements, and other components.

3) Set up the detector (for a gas ionization chamber, this includes setting the gas flow, applying voltages to electrodes, and setting the electronics).

   Steps 1)–3) are performed independently; hence, the order may be changed. In many cases, multiple target wheels are measured sequentially. In such situations, the accelerator and detector systems remain in operation, while only the ion source is shut down, followed by vacuum purging, target wheel replacement, evacuation, and restart of the ion source.

4) Once the vacuum level in the ion source has reached an adequate value, start the ion source, extract the beam, and stabilize it.

(2) Optimization of the measurement equipment

1) Extract ions from the beam adjustment sample and optimize the parameters of the accelerator system so that $^{129}I$ reaches the final detector with maximum efficiency.
2) Optimize the parameters (such as the load voltage and stirring parameters) of the sequential injection system so as to maximize the $^{127}I$ current value in the Faraday cup for stable isotope measurements.

### 7.2.4 Measurement

(1) AMS target preparation

1) Transfer the silver iodide precipitate and metallic niobium powder, with an amount 2.5–4.0 times the weight of the silver iodide precipitate, to an agate mortar. Then, mix thoroughly until a homogeneous mixture is obtained.
2) Press the mixture into target pieces for loading into the ion source. Then, place unknown and standard samples together with beam adjustment and blank samples, as necessary, onto the target wheel. The silver iodide in the samples is extremely hygroscopic. Once pressed into a metal target piece, it immediately begins to adsorb moisture from the atmosphere. While multiple samples are being pressed and placed on the target wheel, the samples are exposed to air. Therefore, the target wheel should be kept in a low-humidity environment during pressing. Further, after pressing is completed, it should be installed in the ion source and evacuation should be performed without delay. If the sample absorbs moisture, cross-contamination is likely to occur in the ion source.

(2) Measurement operation

1) The measurement sequence (the measurement time and number of measurements for unknown samples, measurement time and number of measurements for standard samples, the order of measuring unknown samples, the timing of standard sample measurements, etc.) should be entered into the measurement program in advance. Actual measurements are performed by executing the measurement program.
2) When one measurement is completed and the system moves on to the next sample, the ion current extracted from the new sample requires some time to stabilize. Data acquisition should be performed only after the ion current has stabilized. Hence, preirradiation, which is performed prior to the start of data acquisition, can be specified in the measurement program.
3) One approach to eliminate memory effects between different samples is to irradiate a blank sample between measurements of unknown samples. However, if low-humidity control is properly maintained from sample pressing through installation in the ion source, as described above, this step is unnecessary.

### 7.2.5 Calculation of the $^{129}I/^{127}I$ Atomic Number Ratio

During continuous measurements, a standard material[*444] is measured simultaneously. The measurement results are then normalized using the results of that standard material to determine the $^{129}I/^{127}I$ atomic number ratio $R_{Target}$ of the target.

The $^{129}I/^{127}I$ atomic number ratio of the sample $R_{Sample}$ is calculated according to the following equations:

$$M_C = C \times \frac{W_s}{126.904/N_A} \times 10^{-3}$$

$$M_I = \frac{W}{126.904/N_A} \times 10^{-3}$$

$$R_{Sample} = R_{Target} + (M_I/M_C) \times (R_{Target} - R_{Carrier})$$

$R_{Sample}$ : $^{129}I/^{127}I$ atomic number ratio of the sample

$R_{Target}$ : $^{129}I/^{127}I$ atomic number ratio of the measured target

$R_{Carrier}$ : $^{129}I/^{127}I$ atomic number ratio of the iodine carrier

$C$ : $^{127}I$ concentration in the sample (mg/kg, mg/L, etc.)

$W_s$ : Sample amount (kg, L, etc.)

$W$ : Iodine carrier weight (mg)

[*444] At the Micro Analysis Laboratory, Tandem accelerator, The University of Tokyo (MALT), two standards from the Z94 series (Z94-0596 and Z94-0597) provided by the PRIME Lab of Purdue University (USA) were used as standard samples. Their known isotopic ratios are reported by Sharma (1997) (https://doi.org/10.1016/S0168-583X(96)00675-1). Z94-0596: $^{129}I/^{127}I = 6.3565 \times 10^{-11}$; Z94-0597: $^{129}I/^{127}I = 8.378 \times 10^{-12}$. (Later, the ratio for Z94-0596 was revised to $^{129}I/^{127}I = 6.540 \times 10^{-11}$.) The U.S. National Institute of Standards and Technology (NIST) also provides standard samples with known isotopic ratios. SRM3230 Level I: $^{129}I/^{127}I = 4.920 \times 10^{-10}$; Level II: $^{129}I/^{127}I = 0.985 \times 10^{-12}$.

$M_C$ : Number of $^{127}$I atoms in the sample

$M_I$ : Number of $^{127}$I atoms in the iodine carrier

$N_A$ :Avogadro's number ($6.02 \times 10^{23}$)

### 7.2.6 Calculation of $^{129}$I Radioactivity Concentration

Using the atomic number ratio obtained as per Section 7.2.5 and the $^{127}$I concentration in the sample obtained as per Section 7.1.4 (2), the $^{129}$I radioactivity concentration is calculated using the following equations:

$$M_C = C \times \frac{W_s}{126.904/N_A} \times 10^{-3}$$

$$A = \frac{\ln 2}{T} \times R_{Sample} \times \frac{M_C}{W_s}$$

$R_{Sample}$ : $^{129}$I/$^{127}$I atomic number ratio of the sample

$C$ : $^{127}$I concentration in the sample (mg/kg, mg/L, etc.)

$W_s$ : Sample amount (kg, L, etc.)

$M_C$ : Number of $^{127}$I atoms in the sample

$N_A$ : Avogadro's number ($6.02 \times 10^{23}$)

$A$ : $^{129}$I radioactivity concentration in the sample (Bq/kg, Bq/L, etc.)

$T$ : Half-life of $^{129}$I ($4.95 \times 10^{14}$ s)

## 7.3 Uncertainty

In AMS analyses, the uncertainty of results is generally evaluated by combining the reproducibility error obtained from repeated measurements of standard samples with the statistical error of unknown samples. However, systematic differences in analytical results may occur between different AMS facilities. The primary cause of such discrepancies between facilities is the use of different standard samples. Multiple standard materials are used in $^{129}$I AMS measurements, including the Z-94 series provided by the PRIME Lab at Purdue University (USA), the NIST SRM 3230 series provided by the U.S. NIST, and in-house standards prepared by the Japan Atomic Energy Agency. The assigned values of these standard samples are not necessarily consistent with one another. Therefore, it is important to promote comparisons among AMS facilities to clarify these systematic differences (i.e., differences among standard samples). In addition, as the number of $^{129}$I analyses increases in the future, the gradual consumption or exhaustion of standard samples will become an issue. In the near future, efforts will be required to newly produce common standard samples with agreed assigned values, at least among domestic AMS facilities.

Given these circumstances, it is important to clearly state the standard samples used when reporting analytical results and clarify the possibility of systematic errors caused by the standard samples.

Regarding the uncertainty of analytical results, the pretreatment process involved in AMS target preparation is an important factor. In the case of $^{129}I$ in particular, the differences in iodine chemical forms and behavior during pretreatment between different sample types are not always well understood. It is also important to clarify the processes that cause uncertainties by promoting comparisons among laboratories that perform pretreatment (e.g., processing the same sample and comparing AMS results).

## 7.4 Lower Detection Limit

When considering the detection limits of radionuclides measured by AMS, it is essential to have a thorough understanding of the characteristics of AMS. In AMS, $^{129}I$, which is present in an extremely small amount, is detected by counting individual ions in the detector. Meanwhile, the stable isotope $^{127}I$ is measured as an electric current using a Faraday cup. Therefore, the background in the measurement system is determined by the noise count in the detector and is effectively zero, even over an acceptably long measurement time (for example, approximately 10 hours). However, in actual sample measurements, a carrier is commonly used during pretreatment for many samples. Among currently known carriers, Woodward iodine has one of the lowest $^{129}I/^{127}I$ ratios (reported to be approximately $1–1.5 \times 10^{-14}$). In other words, as long as a carrier is used, this ratio effectively constitutes the practical AMS background. The $^{129}I/^{127}I$ ratio in a target prepared from an actual (unknown) sample is determined by the $^{129}I$ content of the sample, amount of sample used, and amount of carrier added. Near the background level, the measurement uncertainty is determined almost entirely by the count of $^{129}I$ (i.e., statistical counting error). Therefore, the lower limit of detection is defined as the point at which the difference between $^{129}I/^{127}I$ ratio of the unknown sample and that of the blank (target prepared directly from a regular carrier) becomes statistically significant.

Nevertheless, an $^{129}I/^{127}I$ isotopic ratio of $1–1.5 \times 10^{-14}$ is extremely small. For many contemporary environmental samples, it is possible to prepare targets with isotopic ratios significantly higher than this level. For samples containing a sufficiently large amount of $^{129}I$, a more readily available general iodine reagent ($^{129}I/^{127}I = 1.5–1.7 \times 10^{-13}$) can be used as the carrier.

# Chapter 8 Quality Assurance

In addition to performing analysis and measurements in accordance with the procedures described in this document, it is extremely important to ensure traceability to national standards and conduct routine inspections to ensure the integrity of instruments. By continuously implementing these practices, it is possible to demonstrate to third parties that the quality of analytical results is assured. Currently, calculation of the uncertainty of $^{129}$I analysis using AMS is highly dependent on the measurement equipment of each analysis laboratory. Further, the traceability system is generally based on the use of reference samples distributed by international organizations. To ensure the quality of analytical results, it is recommended to follow the principles of ISO/IEC 17025. Quality assurance can be broadly divided into internal quality control conducted by analysts themselves and external quality control, such as by participation in proficiency testing conducted by external organizations.

## 8.1 Internal Quality Control

### 8.1.1 Ensuring Traceability

In $^{129}$I AMS, radioactivity (Bq) and mass (kg) are the quantities for which traceability should be ensured. For the former, traceability should be established for the measuring instrument (AMS device) calibrated using reference materials. For the latter, traceability should be established for electronic balances used in the preparation of measurement samples. In some cases, when the user employs the required reference materials, these materials—traceable to national standards—can be obtained with calibration certificates issued by calibration service providers registered under the Measurement Act. For electronic balances, calibration services provided by the manufacturer can be used. Maintenance and inspection, including the issuance of calibration certificates, should also be performed. Instrument calibration should be performed at appropriate intervals. It is necessary to manage calibration validity periods by setting expiration dates. Confirm in “8.1.2 Routine Inspection” that no change affecting analytical results has occurred in the instrument during the period of validity.

In the same manner, traceability must be ensured for records accompanying analytical results. Specifically, it is important that the collection record sheet that records the date and place of sample collection; the unique number (analysis number, etc.) that identifies the analyzed sample; and various records and forms that are generated during pretreatment, analysis, and measurement operations are managed without gaps.

### 8.1.2 Routine Inspection

Inspection items and methods for equipment used in $^{129}$I AMS are described below. To determine that the instruments are in a proper condition and suitable for use, it is necessary to establish acceptance criteria for each inspection item. It is desirable to establish tentative criteria

with initial data obtained experimentally. After the data are accumulated, the acceptance criteria should be reestablished through statistical processing. It is sufficient to confirm that no changes affecting analysis results have occurred in the instrument; hence, a method different from the one discussed herein may be used. The routine inspection date, person in charge, and inspection results should be recorded.

If the routine inspection results do not meet the acceptance criteria, use of the instrument should be temporarily suspended and the cause should be investigated and resolved. If the cause cannot be resolved by re-measurement or reconfiguration of the instrument by the user, inspection or repair by the manufacturer should be performed.

(1) AMS equipment

Inspect the AMS equipment periodically to ensure that no changes have occurred in the equipment that would affect the analytical results. It is recommended to conduct this inspection each time measurements are performed.

1) Items to be checked during instrument start-up

・Power source

・Gas

・Operation of the PC and analysis software

2) Quantities to be checked during instrument adjustment

・Sensitivity

・Instrument background

3) Measurement of reference materials

・Check variations in measurement results for reference materials

(2) ICP–MS

Inspect the ICP–MS device periodically to ensure that no changes have occurred in the instrument that would affect the analytical results[*445]. It is recommended to conduct this inspection each time measurements are performed.

1) Items to be checked during instrument start-up

・Power source

・Gas

・Operation of the PC and analysis software

[*445] For details, refer to “JIS K 0133: 誘導結合プラズマ質量分析通則 (2022).”

2) Quantities to be checked during instrument adjustment

・Sensitivity

・Instrument background

・Formation ratios of oxide ions and divalent ions

・Short-term stability

・Mass resolution

3) Confirmation of the calibration curve

・Verify the linearity of the calibration curve

(3) Electronic balance

Inspect the electronic balance periodically to ensure that no changes have occurred in the instrument that would affect the analysis results. It is recommended to conduct preuse inspection each time the balance is used along with periodic inspections on a monthly basis or at similar intervals.

・Preuse inspection

This inspection is performed before using the balance. For balances equipped with an internal calibration weight, it is advisable to perform internal calibration in advance. Using a calibration weight close to the mass of the actual sample (or to the lower limit of the usable range)[*446], perform the preuse inspection of the electronic balance and confirm that the weighing result is within the acceptance criteria[*447]. Performing the same inspection after using the balance is also recommended.

・Periodic inspection

Using a calibration weight with a mass close to the maximum weighing capacity of the electronic balance, verify the sensitivity of the balance. For balances equipped with an internal calibration weight, it is advisable to perform internal calibration in advance. The grade of the calibration weight and the acceptance criteria may follow those used for the preuse inspection. This inspection should be performed at fixed intervals. It is recommended to perform it approximately once per month.

[*446] Calibration weights with a calibration certificate (OIML (JIS) Class F2 or higher) are desirable.

[*447] Although the acceptance criteria should be determined based on weighing uncertainty, the minimum weighing value, and a safety factor, an initial control range of 0.5% may be adopted (e.g., when using a 10-g calibration weight, the acceptance criteria would be 9.95–10.05 g.)

(4) Micropipettes

Inspect the micropipettes periodically to ensure that no changes have occurred that would affect the analysis results. It is recommended to conduct preuse inspection each time the micropipettes are used.

・Preuse inspection

Using the micropipette, dispense 1 mL of ultrapure water and weigh it with an electronic balance. Adjust the micropipette so that the measured mass is 1 g. Confirm that the weighing result falls within the acceptance criteria specified in the calibration certificate for the micropipettes.

For micropipettes, periodic inspections should also be conducted once a year by the manufacturer or other qualified organization.

(5) Management of reagents and reference materials

Reagents and reference materials that have a guaranteed shelf life should be used within that period. For those without a specified shelf life, quality control should be ensured by managing information such as the date of opening and other relevant records.

## 8.2 External Quality Control

### 8.2.1 Interlaboratory Comparison

The validity of the measurement and analysis process can be confirmed by conducting a comparison analysis with another laboratory using the same sample and confirming that there is no significant difference between the results of the two analyses.

### 8.2.2 Proficiency Test

By participating in proficiency test programs conducted by external organizations (preferably organizations accredited to ISO/IEC 17043) and comparing the analytical results of test items with the assigned (reference) values, a laboratory can objectively demonstrate its competence.

In proficiency testing conducted in accordance with ISO/IEC 17043, performance evaluation metrics such as Z-scores and En-scores are used to evaluate the performance of participating laboratories.

# Explanation

# Explanation A $^{129}$I Analytical Reference Materials

The use of reference materials is essential for evaluating analytical methods and values. Reference materials are used not only for the evaluation of analytical results but also for the calibration of measurement instruments, value assignment of samples and reagents, and control of analytical precision and processes. According to ISO Guide 34:2009 (JIS Q 17034:2018), reference materials are classified into reference materials (hereinafter referred to as “RM”) and certified reference materials (hereinafter referred to as “CRM”). An RM is a material that is sufficiently homogeneous and stable with respect to one or more specified properties and has been prepared to be suitable for its intended use in a measurement process. A CRM is a reference material characterized using a metrologically valid procedure and accompanied by a certificate stating the value of the specified property, the associated uncertainty, and metrological traceability. CRMs are used to ensure the traceability of measurement results.

Table III.A.1 lists reference materials provided by international analytical organizations that can be used for $^{129}$I analysis by AMS.

Table III.A.1 Reference materials provided for $^{129}I$ ($^{127}I$) analysis※1

| Reference material | Distributing agency | Issue number | Grade | $^{129}I/^{127}I$ | $^{129}I$ concentration | $^{127}I$ concentration | Remarks |
|---|---|---|---|---|---|---|---|
| Seawater | IAEA | 418[*448] | CRM | | $3.2 \pm 0.3 \times 10^{-7}$ Bq/L | | Certified value ($^{129}I$ concentration) (k = 2) |
| Soil (Chernobyl) | IAEA | 375[*449] | RM | $1.72 \times 10^{-7}$ | 0.0017 ± (0.0013–0.0021) Bq/kg | 1.47 ± 0.08 mg/kg | Recommended value ($^{129}I$ concentration) (95% CI) |
| Soil (San Joaquin) | NIST | 2709a[*450] | SRM | $2.3 \times 10^{-10}$ | 6.5 ± 2.6 mBq/g | 4.7 ± 0.5 mg/kg | (Reference) Paper value |
| Sediment (Bikini Atoll) | IAEA | 410[*451] | CRM | $1.35 \pm 0.34 \times 10^{-10}$ | $1.3 \pm 0.04 \times 10^{-5}$ Bq/kg | 0.015 $\mu$g/mg | (Reference) Paper value |
| Sediment (Pacific Ocean) | IAEA | 412[*452] | CRM | | 0.000299 ± 0.000090 Bq/kg | | Information value ($^{129}I$ concentration) (k = 2) |
| Sediment (Buffalo River) | NIST | 8704[*453] | RM | | Bq/kg | 3.97 ± 0.10 mg/kg | (Reference) Paper value |
| Sediment (Freshwater Lake) | NIST | 4354[*454] | | | 0.0774 ± 0.0285 to 0.0850 ± 0.0665 Bq/kg | 7.075 ± 0.567 (approximately) 3.1 $\mu$g/g | (Reference) Paper value |
| Sediment (Ocean) | NIST | 4357[*455] | SRM | (4.16 ± 0.452 to 4.88 ± 0.1945) $\times 10^{-8}$ | 1.05 ± 0.0281 to 1.14 ± 0.0931 mBq/kg | $\mu$g/g | (Reference) Paper value |
| Kelp powder | NIST | 3232[*456] | SRM | | | 944 ± 88 mg/kg | Certified value ($^{127}I$ concentration) (k = 2) |
| Seaweed (Fucusulosus) | IAEA | 446[*457] | CRM | $8.3 \pm 1.3 \times 10^{-8}$ | 0.13 ± 0.02 mBq/g | 0.23 $\mu$g/mg | (Reference) Paper value |
| Seaweed (Radionuclide Standard) | NIST | 4359[*458] | SRM | 2.02 to 2.71 $\times 10^{-9}$ | 0.0148 to 0.0151 mBq/g<br>0.0142 ± 0.05 mBq/g | 1.098 $\mu$g/mg | Information value ($^{129}I$ concentration)<br>(Reference) Paper value |
| Oyster tissue | NIST | 1566a[*459] | SRM | | | 4.46 ± 0.42 mg/kg | Recommended value |
| Peach leaves | NIST | 1547[*460] | SRM | | | 0.3 | (Reference) Paper value |
| Tomato leaves | NIST | 1573a[*461] | | | | 0.85 mg/kg | (Reference) Paper value |
| Whole egg powder | NIST | 1845a[*462] | SRM | | | 3.03 ± 0.10 mg/kg | Recommended value |
| Milk Powder | NIST | 8435[*463] | RM | | | 2.3 ± 0.4 mg/kg | Reference value ($^{127}I$ concentration) (95% CI) |
| Milk Powder | NIST | 1549a[*464] | SRM | | | 3.34 ± 0.30 mg/kg | Recommended value |
| Human Milk | NIST | 1953[*465] | RM | | | 193 ± 2 mg/kg | Reference value ($^{127}I$ concentration) (95% CI) |

*1 Some reference materials may be sold out or temporarily unavailable. Check with each distributing agency for the latest information.

[*448] IAEA Reference Sheet, Certified Reference Material IAEA-418, Iodine-129 in Mediterranean Sea Water (2014)
[*449] IAEA Reference Sheet, Reference Material IAEA-375, Radionuclides and Trace Elements in Soil (2000)
[*450] S. Szidat et al: Analysis of iodine-129 in environmental materials Quality Assurance & Applications, Journal of Radioanalytical and Nuclear Chemistry, 244(1), 45-50 (2000)
[*451] Certification of Massic Activities of Radionuclides in IAEA-410 Bikini Atoll Sediment, IAEA Analytical Quality in Nuclear Applications Series, 53 (2018)
[*452] IAEA Reference Sheet, Reference Material IAEA-412, Radionuclides in Pacific Ocean Sediment (2022)
[*453] A.A. Marchetti et al: Determination of total iodine and sample preparation for AMS measurement of 129I in environmental matrices, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 123(1), 352-355 (1997)
[*454] J. Qiao et al: Speciation Analysis of $^{129}I$, $^{137}Cs$, $^{232}Th$, $^{238}U$, $^{239}Pu$ and $^{240}Pu$ in Environmental Soil and Sediment, Applied Radiation and Isotopes, 70(8), 1698- 1708 (2012)
[*455] J. Okeson et al: A comparative study of $^{129}I$ content in environmental standard materials IAEA 375, NIST SRM 4354 and NIST SRM 4357 by Thermal Ionization Mass Spectrometry and Accelerator Mass Spectrometry, Applied Radiation and Isotopes, 126, 54-57 (2017)
[*456] NIST, Certificate of Analysis Standard Reference Material 3232, Kelp Powder (Thallus laminariae) (2019)
[*457] Q. Liu et al: Preliminary Investigation on the Rapid and Direct AMS Measurement of $^{129}I$ in Environmental Samples without Chemical Separation, Radiocarbon, 58(1), 147-156 (2016)
[*458] Q. Liu et al: Preliminary Investigation on the Rapid and Direct AMS Measurement of $^{129}I$ in Environmental Samples without Chemical Separation, Radiocarbon, 58(1), 147-156 (2016)
[*459] NIST Certificate of Analysis, Standard Reference Material 1566a Oyster Tissue (1989)
[*460] NIST Certificate of Analysis, Standard Reference Material 1547 Peach Leaves (2022)
[*461] R. R. Rao et al: Microwave acid digestion and preconcentration neutron activation analysis of biological and diet samples for iodine, Analytical Chemistry, 63(13), 1298–1303 (1991)
[*462] NIST Certificate of Analysis, Reference Material 1845a Whole Egg Powder (2020)
[*463] NIST Certificate of Analysis, Reference Material 8435 Whole Milk Powder (2008)
[*464] NIST Certificate of Analysis, Standard Reference Material@ 1549a Whole Milk Powde (2022)
[*465] NIST Certificate of Analysis, Reference Material 1953 Human Milk (2017)

# Explanation B Atomic Number Ratio of $^{129}I/^{127}I$

The $^{129}I/^{127}I$ atomic number ratio is an effective tracer for investigating the behavior of iodine in the natural environment. This $^{129}I/^{127}I$ atomic number ratio sensitively reflects even small increases in the $^{129}I$ concentration in a sample and serves as an excellent indicator for simple and quantitative monitoring of the $^{129}I$ concentration. It is important to use the $^{129}I/^{127}I$ atomic number ratio as a tracer for studying iodine behavior in nature.

$^{129}I$ occurs in the natural environment from both natural and anthropogenic sources, including cosmic-ray-induced nuclear reactions, nuclear weapons tests, releases from nuclear fuel reprocessing plants, and nuclear power plant accidents. Currently, emissions from nuclear fuel reprocessing plants constitutes the main source (Table III.B.1). Therefore, the $^{129}I/^{127}I$ atomic number ratio is extremely important for assessing facility contributions to the release and accumulation of $^{129}I$.

Table III.B.1 Sources of $^{129}I$ emissions[*466]

| Emission source | Inventory/Release amount (kg) | $^{129}I/^{127}I$ atomic number ratio |
|---|---|---|
| Nature | 250/year | Up to $1 \times 10^{-12}$ |
| Nuclear weapon tests | 57 | From $10^{-11}$ to $10^{-9}$ |
| Releases into the ocean from EU nuclear fuel reprocessing plants (up to 2008) | 5,600 | From $10^{-8}$ to $10^{-6}$ (North Sea and surrounding waters) |
| Releases to the atmosphere from EU nuclear fuel reprocessing plants (up to 2007) | 440 (Gas) | From $10^{-8}$ to $10^{-6}$ (Rainwater, rivers, and lakes in Western Europe) From $10^{-6}$ to $10^{-3}$ (Soil and vegetation around facilities) |
| Atmospheric releases from the Hanford nuclear fuel reprocessing plant | 275 | From $10^{-6}$ to $10^{-3}$ (Atmosphere around the facility) |

[*466] X. Hou et al.: A review on speciation of iodine-129 in the environmental and biological sample, Analytica Chimica Acta, 632(2), 181-196 (2009)

| | | |
|---|---|---|
| Chernobyl nuclear power plant accident | 1.3–6 | From $10^{-8}$ to $10^{-6}$ (Contaminated area) |
| Fukushima Daiichi Nuclear Power Plant accident (release into the atmosphere)[*467] | From 0.79 to 1.1 | From $10^{-8}$ to $10^{-7}$ |

[*467] M. Honda: A compilation of the 10-year studies on $^{129}I$ in the terrestrial environment after the Fukushima Dai-ichi Nuclear Power Plant accident, Chikyukagaku (Geochemistry), 55, 176–192 (2021)

## Explanation C Cross-checking Results

To validate AMS, cross-checking of environmental and standard samples was conducted using the analytical method described herein. The participating institutions were the University of Tokyo and the Japan Chemical Analysis Center.

Seawater collected in the Chiba Prefecture was filtered and placed in 1-L reagent bottles and subsequently used as environmental samples. The results of the cross-checking are presented in Table III.C.1.

Table III.C.1 Cross-checking results of environmental samples

| Sample | Institution | $^{129}I$ (mBq/kg) ※1 | $^{129}I/^{127}I$ Atomic number ratio※1 |
|---|---|---|---|
| Seawater (Chiba) | A | $(2.4 \pm 0.09) \times 10^{-5}$ | $(7.1 \pm 0.02) \times 10^{-11}$ |
| | | $(3.0 \pm 0.10) \times 10^{-5}$ | $(8.8 \pm 0.03) \times 10^{-11}$ |
| | | $(2.6 \pm 0.08) \times 10^{-5}$ | $(7.6 \pm 0.02) \times 10^{-11}$ |
| | B | $(2.6 \pm 0.10) \times 10^{-5}$ | $(7.8 \pm 0.29) \times 10^{-11}$ |

※1 The uncertainties associated with the $^{129}I$ concentration and the $^{129}I/^{127}I$ atomic number ratio are determined by combining the "repeatability error of standard sample measurements" and the "statistical error of repeated measurements of the same unknown sample."

The standard sample IAEA-412 (Pacific Ocean sediment) distributed by the IAEA was used as the cross-check sample. The sample contained approximately 3 g of the material placed in a brown reagent bottle. Cross-checking results are presented in Table III.C.2.

Table III.C.2 Cross-checking results for standard samples

| Sample | Institution | $^{129}I$ (mBq/kg dry matter) ※1 | $^{129}I/^{127}I$ Atomic number ratio※1 |
|---|---|---|---|
| IAEA412*2 (Pacific Ocean sediment) | A | $0.333 \pm 0.011$ | $(1.26 \pm 0.04) \times 10^{-9}$ |
| | | $0.321 \pm 0.008$ | $(1.22 \pm 0.03) \times 10^{-9}$ |
| | | $0.293 \pm 0.010$ | $(1.16 \pm 0.04) \times 10^{-9}$ |
| | B | $0.340 \pm 0.007$ | $(1.28 \pm 0.03) \times 10^{-9}$ |

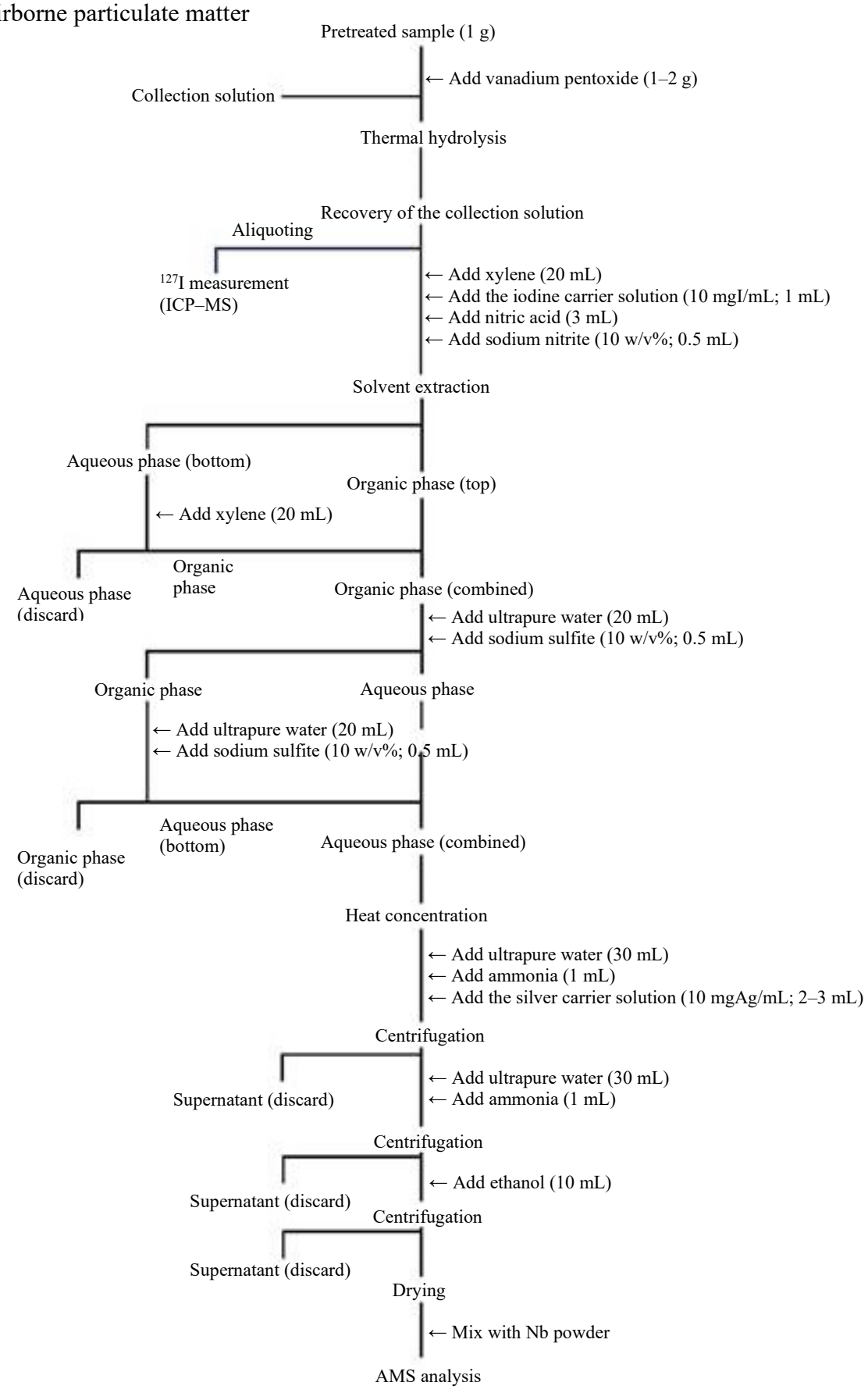
※1 The uncertainties associated with the $^{129}I$ concentration and the $^{129}I/^{127}I$ atomic number ratio are determined by combining the "repeatability error of standard sample measurements" and the "statistical error of repeated measurements of the same unknown sample."

※2 Information value (Bq/kg; based on dry mass): 0.000299 ± 0.000090 Bq/kg (IAEA-412_Rev.05 / 2021-09-16)

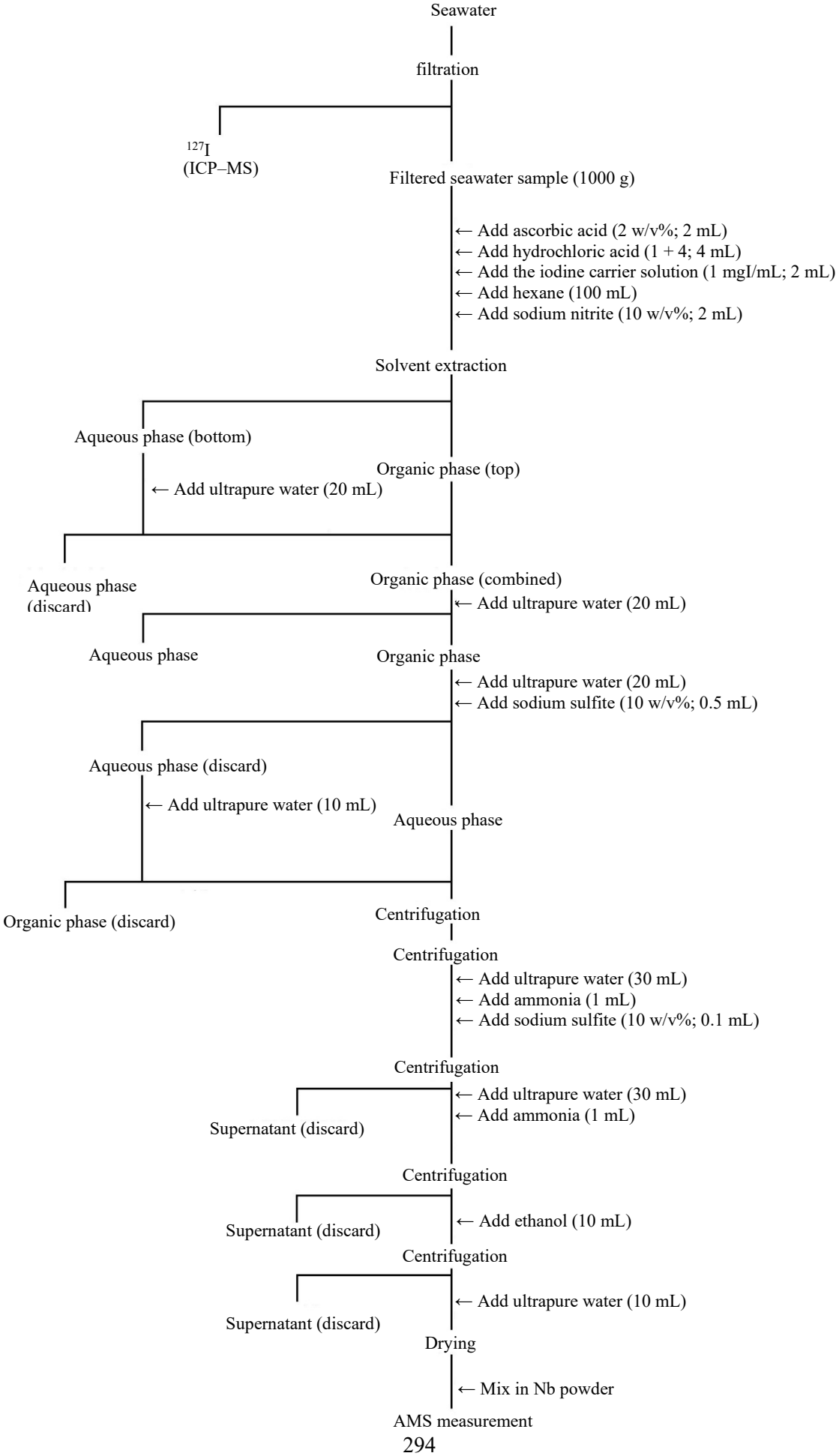
# Appendix

## Analysis Flow

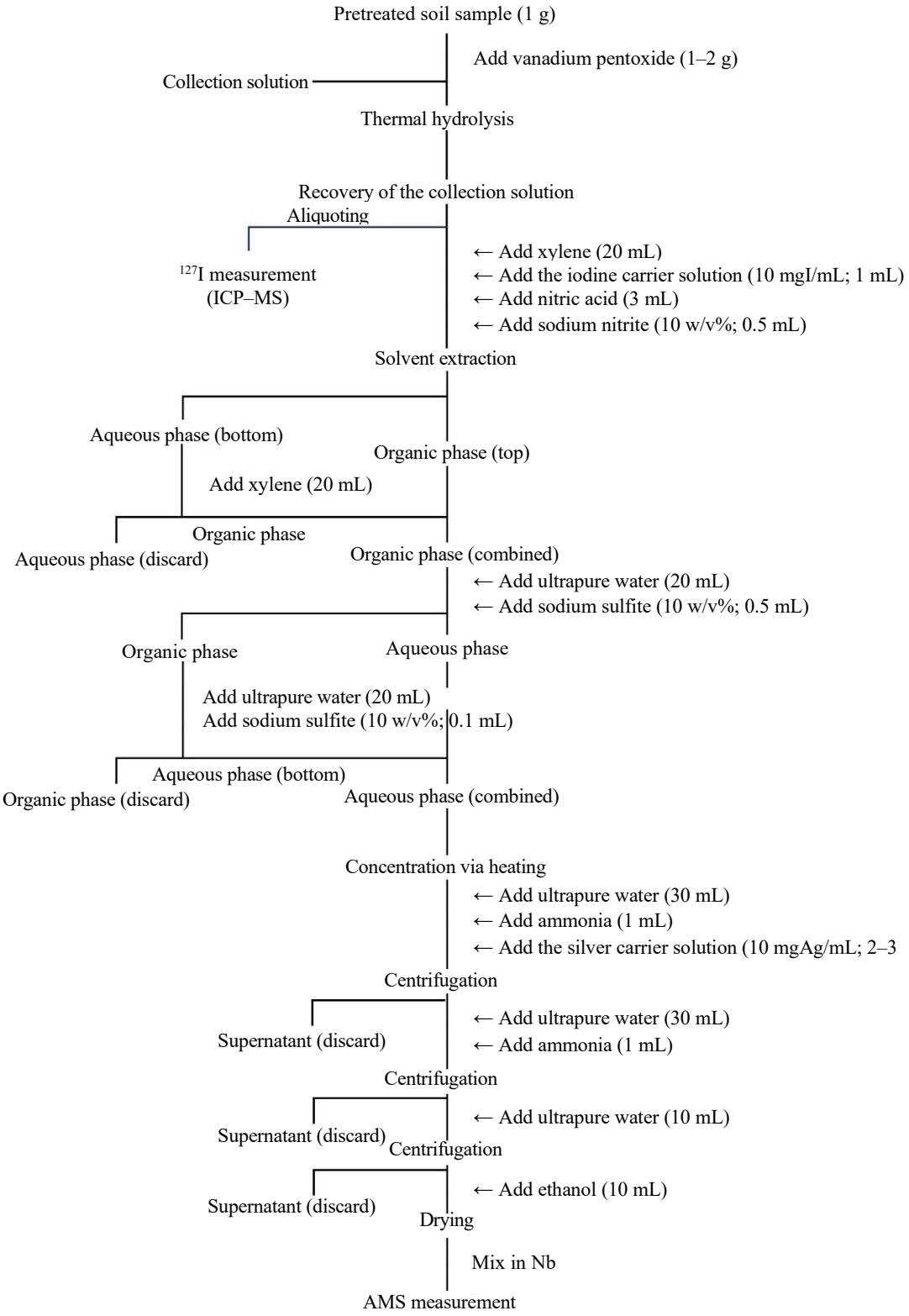
(1) Airborne particulate matter



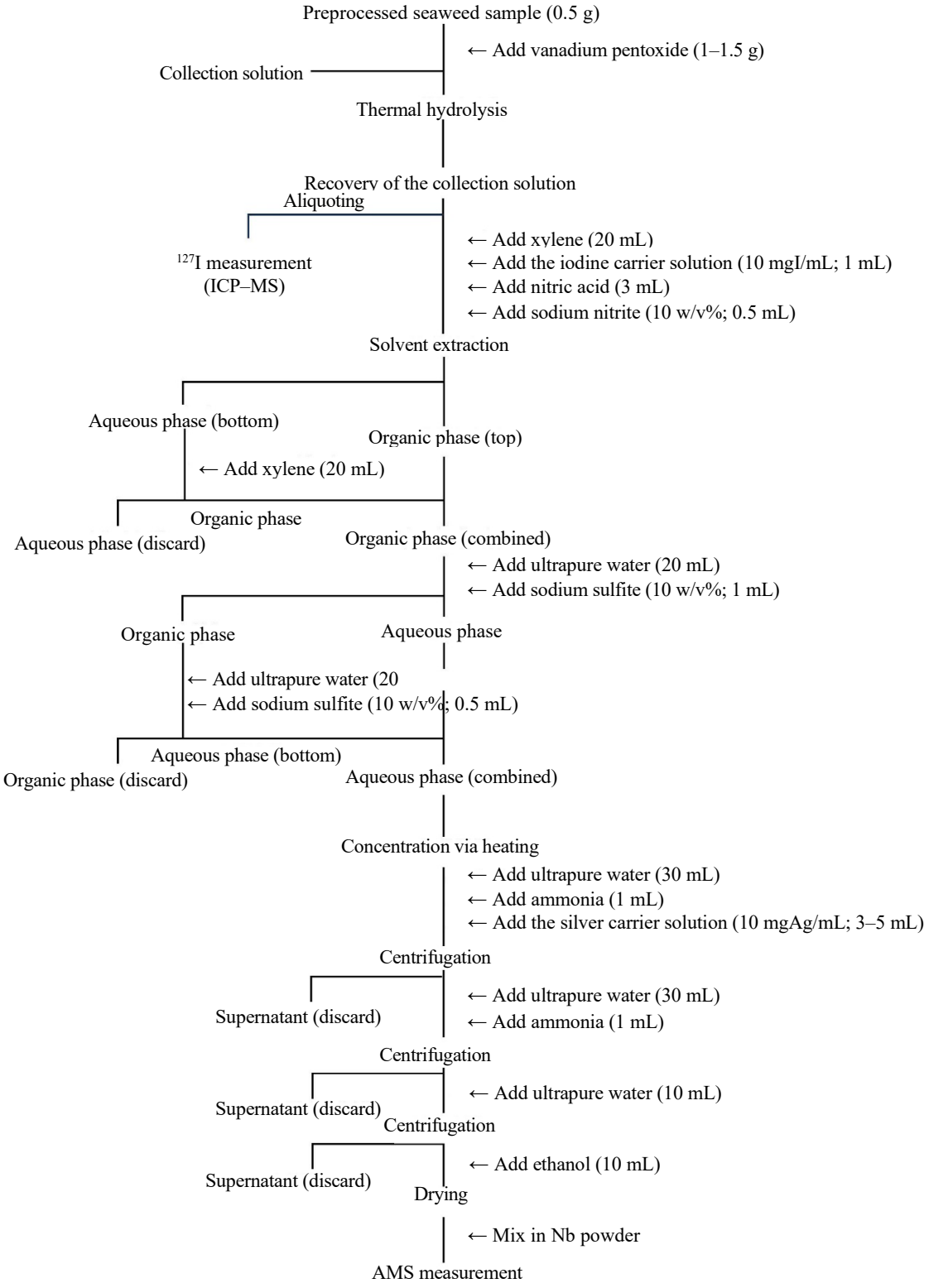
(2) Seawater sample



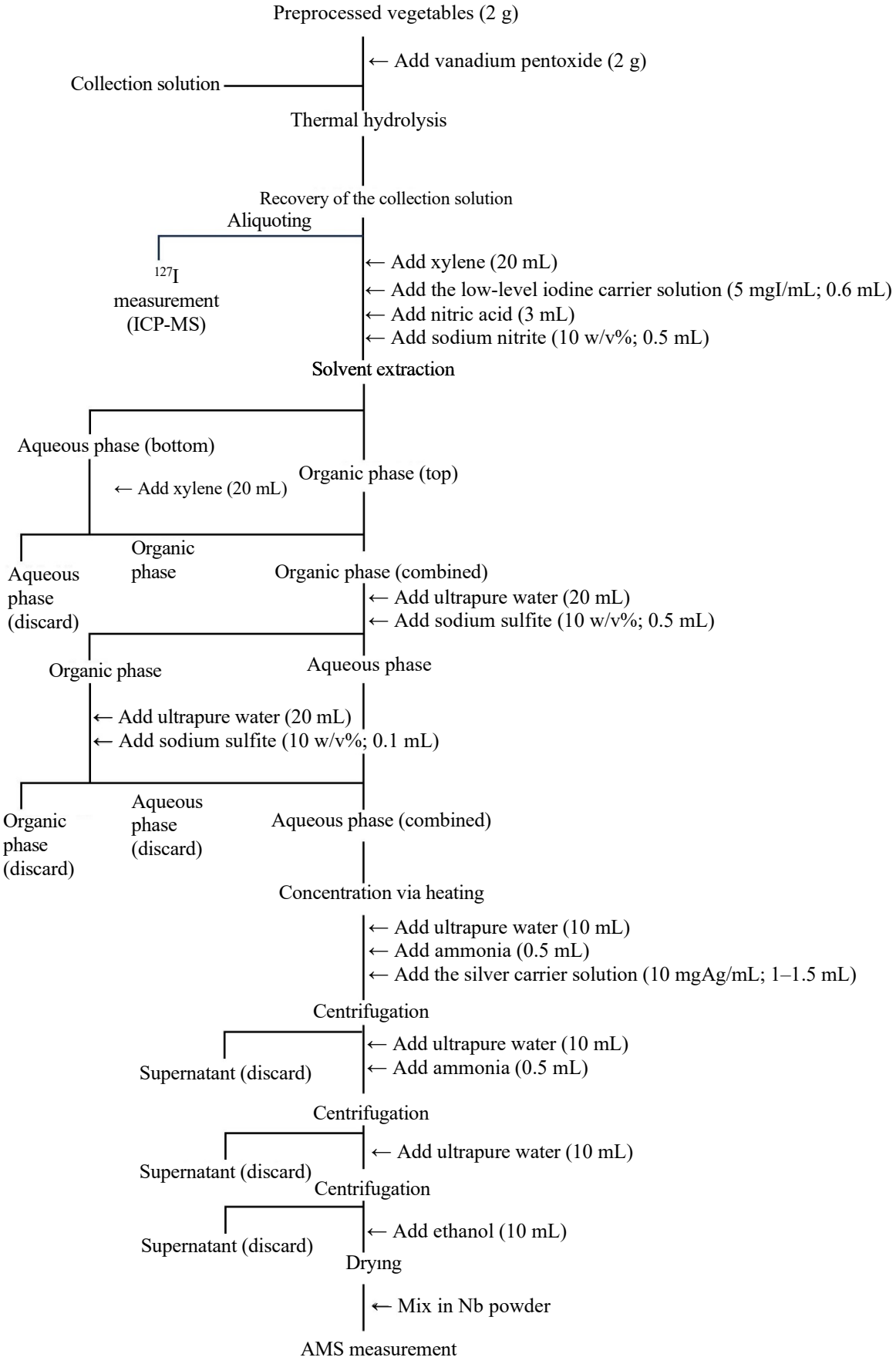
(3) Soil


Pretreated soil sample (1 g)
Add vanadium pentoxide (1–2 g)
Collection solution
Thermal hydrolysis
Recovery of the collection solution
Aliquoting
127I measurement (ICP–MS)
← Add xylene (20 mL)
← Add the iodine carrier solution (10 mgI/mL; 1 mL)
← Add nitric acid (3 mL)
← Add sodium nitrite (10 w/v%; 0.5 mL)
Solvent extraction
Aqueous phase (bottom)
Organic phase (top)
Add xylene (20 mL)
Organic phase
Aqueous phase (discard)
Organic phase (combined)
← Add ultrapure water (20 mL)
← Add sodium sulfite (10 w/v%; 0.5 mL)
Organic phase
Aqueous phase
Add ultrapure water (20 mL)
Add sodium sulfite (10 w/v%; 0.1 mL)
Aqueous phase (bottom)
Organic phase (discard)
Aqueous phase (combined)
Concentration via heating
← Add ultrapure water (30 mL)
← Add ammonia (1 mL)
← Add the silver carrier solution (10 mgAg/mL; 2–3
Centrifugation
Supernatant (discard)
← Add ultrapure water (30 mL)
← Add ammonia (1 mL)
Centrifugation
Supernatant (discard)
← Add ultrapure water (10 mL)
Centrifugation
Supernatant (discard)
← Add ethanol (10 mL)
Drying
Mix in Nb
AMS measurement

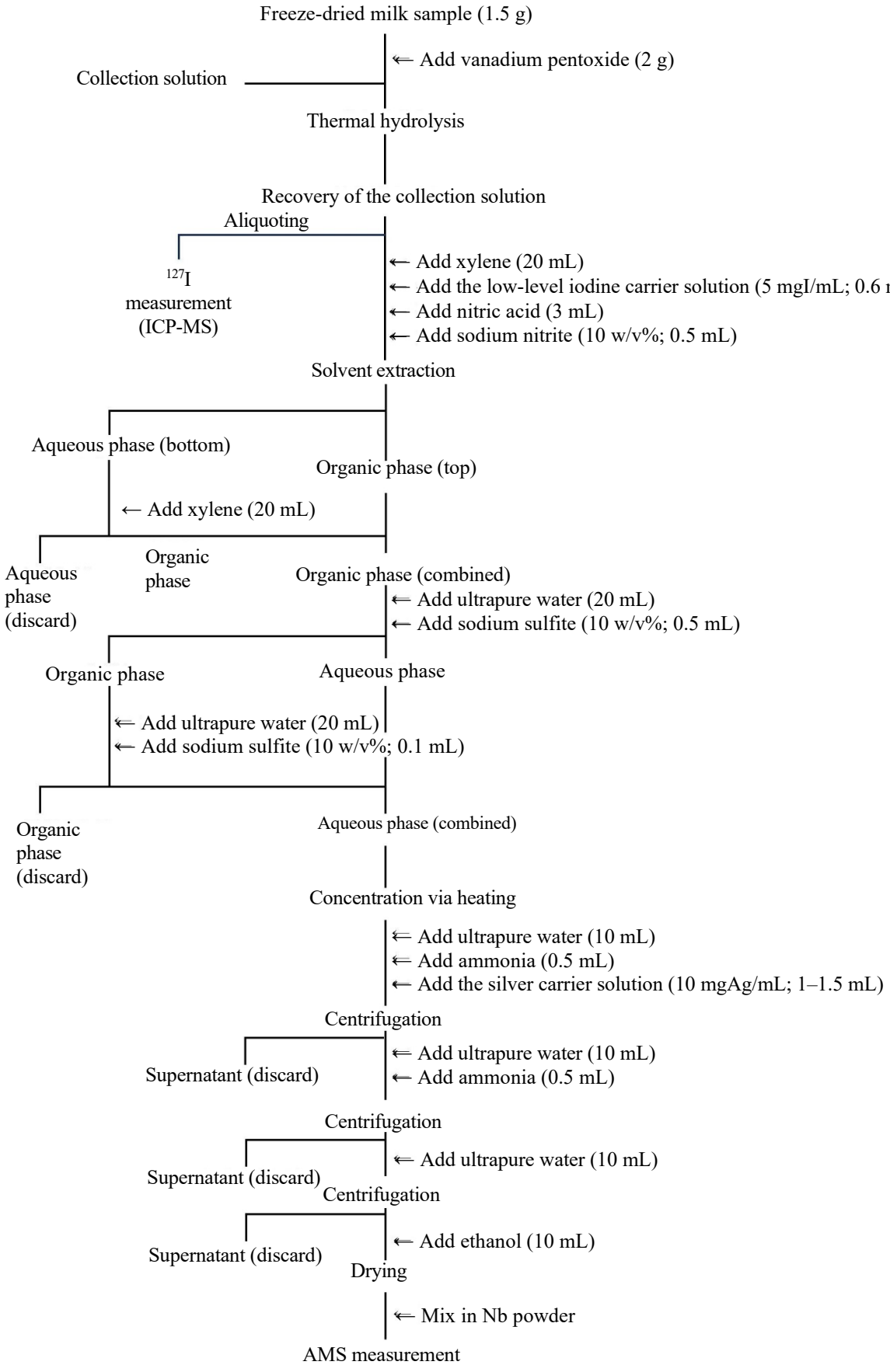
(4) Seaweed


Preprocessed seaweed sample (0.5 g)
← Add vanadium pentoxide (1–1.5 g)
Collection solution
Thermal hydrolysis
Recovery of the collection solution
Aliquoting
$^{127}$I measurement (ICP–MS)
← Add xylene (20 mL)
← Add the iodine carrier solution (10 mgI/mL; 1 mL)
← Add nitric acid (3 mL)
← Add sodium nitrite (10 w/v%; 0.5 mL)
Solvent extraction
Aqueous phase (bottom)
Organic phase (top)
← Add xylene (20 mL)
Organic phase
Aqueous phase (discard)
Organic phase (combined)
← Add ultrapure water (20 mL)
← Add sodium sulfite (10 w/v%; 1 mL)
Organic phase
Aqueous phase
← Add ultrapure water (20
← Add sodium sulfite (10 w/v%; 0.5 mL)
Aqueous phase (bottom)
Organic phase (discard)
Aqueous phase (combined)
Concentration via heating
← Add ultrapure water (30 mL)
← Add ammonia (1 mL)
← Add the silver carrier solution (10 mgAg/mL; 3–5 mL)
Centrifugation
Supernatant (discard)
← Add ultrapure water (30 mL)
← Add ammonia (1 mL)
Centrifugation
Supernatant (discard)
← Add ultrapure water (10 mL)
Centrifugation
Supernatant (discard)
← Add ethanol (10 mL)
Drying
← Mix in Nb powder
AMS measurement

(5) Vegetables



(6) Milk


Freeze-dried milk sample (1.5 g)
⇐ Add vanadium pentoxide (2 g)
Collection solution
Thermal hydrolysis
Recovery of the collection solution
Aliquoting
$^{127}$I measurement (ICP-MS)
⇐ Add xylene (20 mL)
⇐ Add the low-level iodine carrier solution (5 mgI/mL; 0.6 mL)
⇐ Add nitric acid (3 mL)
⇐ Add sodium nitrite (10 w/v%; 0.5 mL)
Solvent extraction
Aqueous phase (bottom)
Organic phase (top)
← Add xylene (20 mL)
Aqueous phase (discard)
Organic phase
Organic phase (combined)
⇐ Add ultrapure water (20 mL)
⇐ Add sodium sulfite (10 w/v%; 0.5 mL)
Organic phase
Aqueous phase
⇐ Add ultrapure water (20 mL)
⇐ Add sodium sulfite (10 w/v%; 0.1 mL)
Organic phase (discard)
Aqueous phase (combined)
Concentration via heating
⇐ Add ultrapure water (10 mL)
⇐ Add ammonia (0.5 mL)
⇐ Add the silver carrier solution (10 mgAg/mL; 1–1.5 mL)
Centrifugation
Supernatant (discard)
⇐ Add ultrapure water (10 mL)
⇐ Add ammonia (0.5 mL)
Centrifugation
Supernatant (discard)
⇐ Add ultrapure water (10 mL)
Centrifugation
Supernatant (discard)
⇐ Add ethanol (10 mL)
Drying
⇐ Mix in Nb powder
AMS measurement

# Common Appendix and References

# Common Appendix A Nuclear Data and Decay Scheme of $^{129}$I

In this measurement method, the nuclear data for $^{129}$I obtained from the Evaluated Nuclear Structure Data File (ENSDF) published by the U.S. National Nuclear Data Center (NNDC) are used, as summarized in Table 1.1.

Appendix Table 1.1 Nuclear data for $^{129}$I ※1,※2

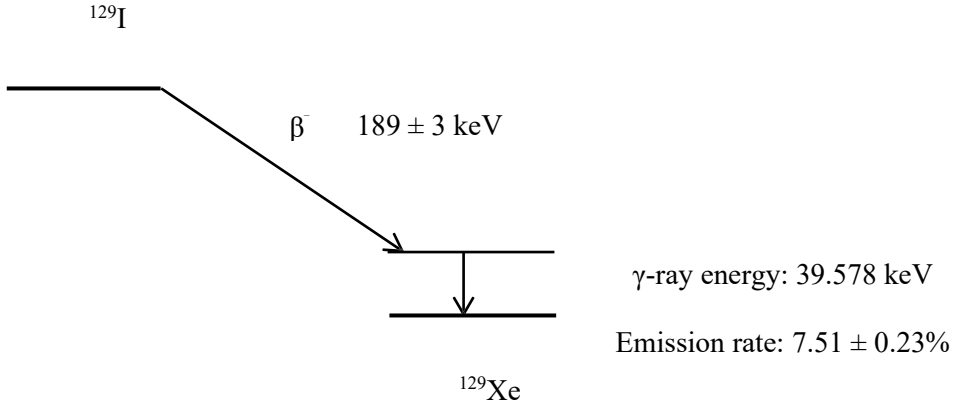
| Half-life (years) | Maximum β-ray energy (keV) | Decay mode (Emission probability) |
|---|---|---|
| $(1.57 \pm 0.04) \times 10^7$ | 189 ± 3 | $\beta^-$ (100%) |

※1 The source of the nuclear data is the ENSDF (as of November 2023).

※2 The half-lives and maximum β-ray energies are listed with their uncertainties.

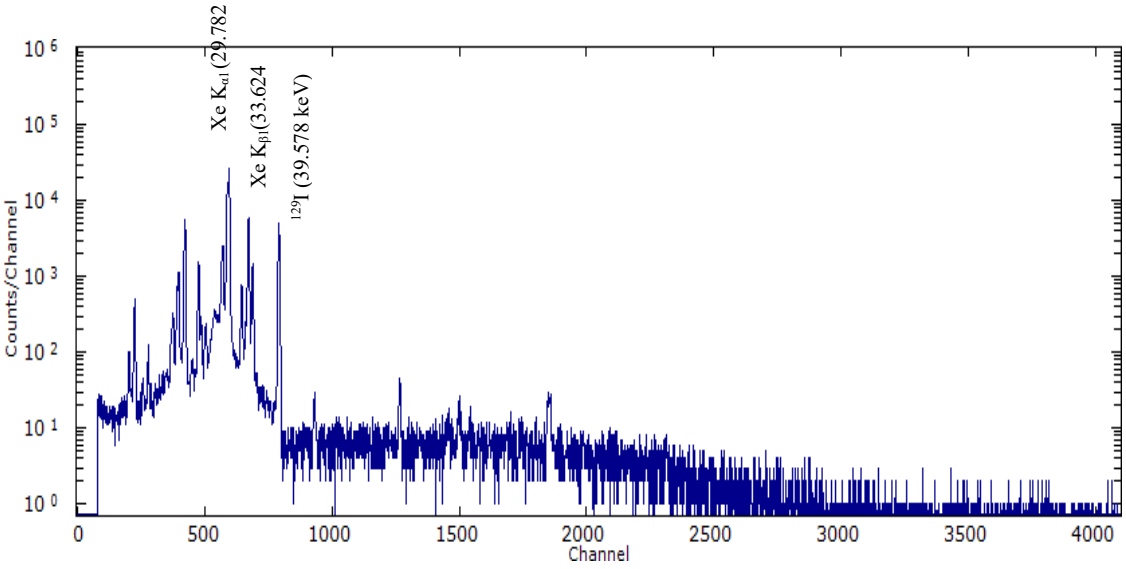
The decay scheme of $^{129}$I is shown in Appendix Figure 1.1. After $\beta^-$ decay, $^{129}$I transitions to the excited state $^{129}$Xe. Subsequently, 7.51 ± 0.23% of the decays emit a γ-ray with an energy of 39.578 keV while 92.33% proceed via internal conversion, emitting internal conversion electrons. Therefore, when $^{129}$I is measured using a low-energy photon spectrometer, peaks corresponding to Xe X-rays (e.g., $K_{\alpha 1}$: 29.782 keV and $K_{\beta 1}$: 33.624 keV) are observed.

In addition, when γ-rays emitted from excited $^{129}$Xe interact with germanium in the detector and the resulting germanium X-rays (e.g., Kα1: 9.886 keV) escape from the detector, X-ray escape peaks appear at energies such as 29.692 keV.




Appendix Figure 1.1 Decay scheme of $^{129}$I

An example spectral diagram measured for 80,000 seconds using a low-energy photon spectrometer is shown in Appendix Figure 1.2. The numerical values for γ-ray and X-ray energies were obtained from the Table of Isotopes (8th Edition) and ENSDF.




Appendix Figure 1.2 Example of a spectral diagram measured by a low-energy photon spectrometer

# Common Appendix B Terminology

| Term | Description |
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| Ion-exchange resin | General term for insoluble, porous resins with ion-exchange groups. Used for chemical separation by leveraging the fact that the distribution coefficient for adsorption and desorption of solute ions onto the resin varies depending on the properties of the solvent. |
| Ion meter | An instrument used to measure the concentration of ions in a solution. The concentration is determined from the potential difference produced by the difference in the ion concentration. |
| Counting rate | The number of counts per unit time, usually expressed as cpm (counts per minute) or cps (counts per second). |
| Decision threshold | The boundary value of the background distribution corresponding to the probability α of a Type-I error (i.e., the probability of incorrectly concluding that a physical effect is present in the background measurement) when calculating the detection limit in accordance with ISO 11929. |
| Lower detection limit | The minimum amount that can be detected. The Kaiser method, ISO 11929 (Currie method), and the Cooper method are used to calculate the lower detection limit. |
| Primary estimate | A mathematical estimate of the statistically most probable value. In ISO 11929, this corresponds to “primary estimate.” |
| Carrier | A large amount of material added when handling extremely small numbers of radioactive nuclide atoms, for example during precipitation. Herein, it refers to the stable isotope added during the separation or extraction of radionuclides. |
| Liquid–liquid extraction and back-extraction | The operation of separating a solute by transferring it from an aqueous phase to an organic phase that has a higher affinity for the solute is called extraction or liquid–liquid extraction. Conversely, transferring a solute from the organic phase back into the aqueous phase is called back-extraction. |
| Decantation | An operation of separating the supernatant by gently tilting the vessel after allowing the generated precipitate to settle. |

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| Half-life | The time required for radioactivity to decrease to one-half of its value at a certain reference time.<br>The half-life is intrinsic to each nuclide and ranges from far less than 1 second to billions of years. If the half-life is $T$, the elapsed time is $t$, and the radioactivity at the reference time ($t$ = 0) is $A_0$ the radioactivity $A$ at time $t$ is expressed as follows:<br>$A = A_0 e^{-\lambda t}$ OR, $A = A_0 \left(\frac{1}{2}\right)^{t/T}$<br>The relationship between the half-life $T$ and the decay constant $\lambda$ is $T = \ln(2)/\lambda$, with $\ln(2) \fallingdotseq 0.693$. |
| Uncertainty | The range of variation that a measured result may statistically show. It is obtained by combining uncertainties related to counting (conventionally called the "counting error"), measurement efficiencies, weighing of sample amounts, and other inputs used to obtain the measurement value. |
| $E_n$ score | One of the methods of evaluating the skills of a testing laboratory. The score is expressed by the following equation. If the absolute value is <1, the performance is considered satisfactory.<br>$En = \frac{\text{Analysis value}_{lab} - \text{Analysis value}_{ref}}{\sqrt{U_{lab}{}^2 + U_{ref}{}^2}}$<br>$Ulab$: Expanded uncertainty of the participating laboratory (inclusion factor k = 2)<br>$Uref$: Expanded uncertainty of the reference laboratory or assigned value (inclusion factor k = 2) |
| ICP–MS | Abbreviation for inductively coupled plasma–mass spectrometry.<br>The analyte elements contained in the sample are ionized by an inductively coupled plasma (ICP), the resulting ions are introduced into a mass analyzer, and then the elements or isotopes are analyzed by measuring the number of ions at the *m/z* value corresponding to the analyte. |
| Triple quadrupole ICP–MS | ICP–MS with two quadrupole mass filters in series (MS/MS arrangement) and a collision reaction cell between them. |
| Collision Reaction Cell (CRC) | Abbreviation for a collision reaction cell. A cell designed to reduce or remove ions causing spectral interference (e.g., polyatomic or molecular ions) by colliding ions with specific gases (e.g., helium) and/or reacting ions with certain gases (e.g., hydrogen, oxygen, methane, and ammonia). |
| *m/z* | A symbol representing the dimensionless quantity obtained by dividing the ion mass by the unified atomic mass unit and then by the ion charge number. It is the mass-to-charge number ratio. |

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| Spectral Interference | A phenomenon in which signals originating from the solvent, coexisting elements, or the plasma of the ion source (such as isobars, polyatomic ions, molecular ions, or multivalent ions) overlap with the mass spectral signal of the target element or isotope. |
| Internal-standard element | An element added to the calibration blank solution, calibration standard solution, procedural blank solution, and sample solution to correct for nonspectral interferences and time-dependent sensitivity drift in ICP–MS. |
| Memory effect | A phenomenon in which elements contained in previously analyzed samples or calibration standard solutions remain within the ICP–MS instrument or its auxiliary components, and a portion of them appears superimposed on the signal of the analyte element in the sample currently being measured. |
| Sample introduction system | A system used to introduce liquid samples into the ICP. It consists of a nebulizer and a spray chamber. The spray chamber allows only fine aerosol droplets generated by the nebulizer to pass. |
| Nebulizer | A component that atomizes liquid samples via high-pressure, high-velocity gas flow. |
| Lower detection limit (triple quadrupole ICP–MS) | The minimum detectable amount (value). In ICP–MS analysis, this is calculated using the evaluation method specified in JIS K 0133. |
| Instrument detection limit | One of the lower detection limits. It is the lowest concentration that an instrument can detect. It is defined as the concentration corresponding to three times the standard deviation of signals obtained by measuring a calibration blank solution 10 times. |
| Method detection limit | One of the lower detection limits. It is the lowest concentration that can be detected by an analytical method. It is defined as the concentration corresponding to three times the standard deviation of signals obtained by measuring a procedural blank solution 10 times. |
| Calibration curve | The relationship line obtained by plotting the concentration of the calibration blank solution and calibration standard solution containing the analyte on the horizontal axis and the signal intensity (counting rate) on the vertical axis. The concentration range for the calibration curve should ensure a linear relationship between signal intensity and concentration and should encompass the concentration of the element in the sample solution to be measured. |
| Calibration blank solution | A solution with the same properties as the calibration standard solution but without the analyte element. |
| Procedural blank solution | A solution processed in exactly the same manner as the sample but without the sample. Used to evaluate the presence or absence of |

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| | contamination of the target element or interfering elements from the laboratory environment, reagents, and instruments. |
| Pre and postmeasurement blanks | Calibration blank or rinse solutions measured before and after the sample solution. Used to evaluate memory effects in the instrument. |
| Background | The signal of a target element or isotope obtained when a calibration blank solution is introduced. This signal combines instrument background, spectral interferences, and nonspectral interferences. |
| Instrument background | The signal received by the ion detector due to electrical noise and light from the ICP. Also called “dark current.” |
| Abundance sensitivity | An indicator used to check the influence of adjacent peaks when present, for example in samples with a large number of principal components and matrices. |
| Background Equivalent Concentration (BEC) | Abbreviation for background equivalent concentration. The concentration of the target element that gives a signal intensity equal to the background intensity. |
| w/v% | Mass percentage concentration. |
| Tandem accelerator | A type of accelerator that uses electrostatic field to accelerate ions in two stages. First, negative ions are accelerated toward the middle of the accelerator tube where a high voltage is applied. After the negative ions are converted into positive ions in the high-voltage terminal, positive ions are further accelerated. |
| Negative ion source | In a tandem accelerator, a source in which thermally ionized $Cs^+$ is directed onto the sample surface. Atoms sputtered from the sample interact with $Cs^+$ to generate a negative ion current. |
| Low-level iodine carrier | A carrier with an $^{129}I/^{127}I$ atomic number ratio on the order of $10^{-14}$. |

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