Users' Manual

# Training package for mercury monitoring to enhance national capacity to generate internationally comparable scientific data

Ver. 1.0

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UN environment programme

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# EXECUTIVE SUMMARY

Mercury is a chemical element that has existed on Earth since its creation. Mercury is released from natural sources by processes, such as volcanic activity and permafrost melting. In recent years, more mercury has been released through human activities, such as the combustion of fuels, mining activities, and the consumption of mercury-added products. Once emitted to the atmosphere, mercury remains for a long time, and will be transported long distances. Atmospheric mercury is eventually oxidized, and then deposited in the ocean or on land.

Growing concerns for mercury risks have resulted in the adoption and entry into force of the Minamata Convention on Mercury (the Convention). The Parties to the Convention are obliged to inform the Conference of the Parties about the national situation and implementation. There is a growing need for capacity building concerning appropriate mercury monitoring skills in developing countries to ensure the proper implementation of the required efforts under the Convention by monitoring the levels of mercury and mercury compounds.

The 'Training package for mercury monitoring to enhance national capacity to generate internationally comparable scientific data' addresses specific skills for laboratory managers and technicians to produce reliable data. It enhances national capacity to generate scientific data by using multimedia and focusing on different applications that meets internationally acceptable level. The material provides not only manual skills to use devices and instruments, but also information on the principles of quality assurance and quality control to address comparability issues. Quality is the value of produced data. Practical examples to reduce data bias and uncertainty are also provided.

The training package is composed of multimedia files, i.e., videos, which provide substantive information when organizing a training programme. The video material is prepared using Microsoft PowerPoint with pre-recorded narration embedded in each slide and then grouped by deck in each topic/subject. This Users' Manual provides a sample course with full scope that uses the materials in one consistent programme, but the training package does not need to be used in full. The organizer can prepare the 'custom-made' slide decks for its own training programme. The following video lectures are annexed to the Users' Manual:

- Physical and chemical properties, usage, and environmental behaviours
- Atmospheric survey and analysis (manual active sampling method)
- Solid sample (soil, sediment, and biota) survey and analysis
- Water sample survey and analysis
- Human biological sample analysis
- Methylmercury analysis
- Mercury monitoring and the Minamata Convention
- Quality management

- Laboratory safety and environmental management

The main body of the training package covers the specific skills for mercury analysis and laboratory management. It also provides general knowledge on mercury science and its regulatory framework as the foundation and for better understanding of the issue to the audiences who acquires specific skills through this material. However, it is not designed to fit all occasions universally but instead to provides specific information for the audiences who need the practical knowledge and skills on mercury monitoring. Therefore, when designing a training programme, the organizer should firstly develop a conceptual idea for a capacity strengthening activity and consider if any part of this material can benefit the purpose of the activity.

This material provides practical and hands-on information to enable self-study to address needs in an online setting even under travel restrictions such as during the COVID-19 pandemic. Scientists and practitioners of mercury management at national level is the primary target audiences for this material. It can also be used by lecturers or trainers as teaching material as it has been developed with customizable multimedia files to fit to their teaching syllabus.

The training programme can be organized in face-to-face, online, or hybrid settings. In each case, the facilitator(s) will run the programme and guide the audiences / participants to certain direction. Online programmes are an emerging training style which has rapidly developed and expended in the past few years. New online platforms and applications have been introduced and become more versatile. However, mercury monitoring is an activity that involves field sampling and laboratory analysis, which cannot be completed virtually. This training package includes many videos from the field and laboratory so that the participant may also exercise the procedures in a face-to-face setting.

# 1 BACKGROUND

## 1.1 Global mercury issues

Mercury is a chemical element that has existed on Earth since its creation. Mercury is released from natural sources by processes, such as volcanic activity and permafrost melting. In recent years, more mercury has been released through human activities, such as the combustion of fuels, mining activities, and the consumption of mercury-added products.

Once emitted to atmosphere, mercury remains for long time, and will be transported long distances. Atmospheric mercury is eventually oxidized, and deposited in the ocean or on land. As mercury levels in the air, ocean and soil are in equilibrium, more legacy mercury is re-emitted to the atmosphere. Some inorganic mercury in water bodies can be methylated by microbial activities, and bioaccumulated in biota at higher trophic levels. Eventually, fishing brings mercury back to human society through consumption. Excessive exposure to mercury, especially methylmercury, will pose risk to vulnerable population, particularly pregnant women as methylmercury actively passes through placenta barrier by amino acid transporter to fetus.

Due to its environmental behaviours and anthropogenic emissions and releases, growing concerns about mercury risks have resulted in the adoption and entry into force of the Minamata Convention on Mercury (the Convention). It is one of the newest multilateral environmental agreements aiming at protecting human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds.

In October 2013, the Diplomatic Conference on the Convention was convened in Kumamoto City in Japan, with a ceremonial opening in Minamata City, to formally adopt the Convention and open it for signature. It entered into force in August 2017 and the Parties to the Convention must abide by the provisions stipulated in the Convention text.

## 1.2 Context of this Training Package

The Minamata Convention obliges the Parties to take various measures to protect human health and the environment from anthropogenic emissions and releases of mercury. Its preamble also clarifies that the Parties can take additional measures beyond the requirements of the Convention's provisions. To effectively protect human health and the environment from mercury, it is important to understand the levels of mercury in the environment and other matrices, which lead to environmental and human exposure to mercury. Article 19 (research, development, and monitoring) of the Convention requires the Parties to cooperate to develop and improve geographically representative monitoring of the levels of mercury in the environmental media and human populations. Article 18 (public information, awareness and education) also stipulates that each Party shall provide to the public of available information on research, development and monitoring activities under Article 19. Article 16 (health aspects) refers to the monitoring of health risk. Technical guidance developed under specific articles also provides guidance on monitoring, such as artisanal and small-scale gold mining site monitoring under Article 7, emission monitoring under Article 8, and contaminated site monitoring under Article 12. For the effective implementation of the Convention, it is crucial to identify the priority areas from available data concerning the status of trade, use, emission/release and disposal of mercury at the national level and to translate them into domestic policy. Moreover, Article 22 (effectiveness evaluation) requires the Conference of the Parties (COP) to evaluate the effectiveness of the Convention, based on information including monitoring data on the presence and movement of mercury in the environment and human populations. The Parties may also wish to investigate the effectiveness of their domestic measures based on local, national or regional monitoring activities.

There is a growing need for capacity building concerning appropriate mercury monitoring skills in developing countries to ensure the effective implementation of the provisions of the Convention by monitoring the levels of mercury and mercury compounds. Such capacity building can contribute to the prioritization of policies, planning and implementation of mercury control measures and the evaluation of policy measures.

Mercury monitoring requires specific skills for laboratory managers and technicians to produce reliable data. The training package for monitoring laboratories that monitor mercury levels will enhance national capacity to generate scientific data by using multimedia and focusing on different applications that are internationally comparable. The material provides not only manual skills to use devices and instruments, but also information on the principles of quality assurance (QA) and quality control (QC) to address comparability issues. Quality is the value of produced data. Practical examples to reduce data bias and uncertainty are also provided.

## 1.3 Development of this training package

UNEP Regional Office in Asia and the Pacific (ROAP) is implementing a Japan-funded project called “Project for promoting the Minamata Convention on Mercury by making the most of Japan's knowledge and experiences[1]” to support its member states, regardless of the ratification status for the implementation of the Convention.

Most of the presentation materials are developed along with the online training programmes of the project between December 2020 and February 2022. They are primarily developed to support the project partner countries in Asia and the Pacific, but the content can be applied universally beyond the geographical regions and sectors. Building on these materials, the training package can be reconfigured to be relevant to more generic needs so that it can be distributed and made available globally.

The training package is composed of multimedia files, i.e., videos, which provide substantive information when organizing a training programme. The video material is prepared using Microsoft PowerPoint with pre-recorded narration embedded in each slide, then grouped by deck in each topic/subject. All contents were compiled into a form of ‘Users’ manual’, which includes not only the presentation videos but also sample training course, pre- and post-training self-test and evaluations, and the background information. This training package enables users to customize their own training programmes by selecting, adding, or modifying the contents. It can easily integrate the additional cross-cutting issues such as gender and human rights available in the reference literature section.

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[1] Project makes special focus in the area of information exchange (Article 17), awareness and education (Article 18), and research, development and monitoring (Article 19) to contribute the early implementation of the Convention. A comprehensive programme is designed to strengthening enabling capacity, building on the resources in and around Minamata, and employing technologies held by institutions in Japan.

# 2 INTRODUCTION

## 2.1 Purpose

This document intends to support the Parties and stakeholders to enhance mercury monitoring and analytical capacity to contribute to the prioritization of policies, planning and implementation of mercury control measures and the evaluation of the implemented policies.

The Minamata Convention includes a number of specific provisions related to mercury monitoring. Firstly, Article 19 provides for cooperation among the Parties on research, development, and monitoring. The geographically representative monitoring of levels of mercury and mercury compounds in vulnerable populations and in environmental media is encouraged particularly in a collaborative manner for the collection and sharing of such samples.

Secondly, Article 16 provides for the monitoring of health risks related to the exposure to mercury and mercury compounds by strengthening institutional and individual capacities in the health sector.

Thirdly, Articles 18 requires the Parties to promote and facilitate the provision of the monitoring results to the public.

Fourthly, Article 22 requires that the monitoring information is utilized to evaluate the effectiveness of the Convention. In particular, comparative and representative monitoring data, both spatially and temporally, will be a very useful information for the COP to examine the global situation and impact of the intervention. The COP prepared scientific and technical guidance to obtain comparable monitoring data to evaluate the effectiveness of the Convention.

This document is expected to support the Parties in generating comparable monitoring data as stipulated in the articles above. The document will also support governments, academia, and other organizations to develop and improve QC and QA mechanisms throughout its operation procedures.

This material provides practical and hands-on information with multimedia files (video) to enable their self-study to address their needs in online setting even under the travel restriction such as COVID-19 pandemic. Scientists and practitioners of mercury management at the national level are the primary target audiences for this material. It can also be used by lecturers or trainers as their teaching material as it is developed with customizable multimedia files to fit to their teaching syllabus.

## 2.2 Limitation

Mercury issues are diverse and the needs on each occasion of different countries are significantly different. This training package provides knowledge and skills at intermediate level with relatively limited timeframe. For further advancement, additional capacity strengthening programmes should be organized in order to address the specific knowledge and skills which are beyond the scope of this training package.

In addition, this training will not completely replace the face-to-face or hands-on training, which can provide more comprehensive and intensive capacity strengthening opportunities. This material will sufficiently cover the environmental and biological media, where human health and environmental conservation are of concern. There is also a need for mercury monitoring in other media, for example, the mercury content in products should be monitored for law compliance checks. However, the methodologies and necessary instruments are very different, so these items are not covered.

# 3 TRAINERS' GUIDANCE

## 3.1 Course design

The needs of capacity strengthening are diverse. Numerous activities are developed and implemented by many organizations and individuals. Before developing a training programme, it is essential to recognize its purpose and logical relation towards the problem that the training programme is going to address. The objective, or desired outcome, is the most important motives for developing a training programme. The needs of the audiences are another important aspect that should be appropriately assessed or set as the first step of the programme development. If the audiences are the internal staff of an organization, the capacity strengthening needs would be aligned with its short- or long-term strategy and should be systematically addressed. It is recommendable to develop a concept note that outlines the background, objective, and key arrangement. The concept note will be shared among stakeholders and discussed for elaborating the training course in detail.

The 'training package for mercury monitoring to enhance national capacity to generate internationally comparable scientific data' can serve as the substantive input to the activities either partially or entirely.

This material is configured with lectures and supplemental materials on general knowledge and specific skills (Table 1). The main body of the training package covers the specific skills on mercury analysis and laboratory management. It also provides general knowledge on mercury science and its regulatory framework as the foundation and for better understanding of the issues by the audiences who acquires specific skills through this material. However, it is not designed to fit all occasions universally but provides specific information for the audiences who need the practical knowledge and skills on mercury monitoring. Therefore, when designing a training programme, the organizer should firstly develop a conceptual idea for a capacity strengthening activity and consider if any part of this material can benefit the purpose of the activity. It is particularly the case for the cross-cutting topics such as gender and human rights, which could be underlined throughout the programme concept. Key reference literatures are developed by Strategic Approach to International Chemicals Management (2017), UNEP (2016), and UNEP and Minamata Convention (2021) and available online. They will provide the fundamental concept of the human-environment interactions in line with the principle of 'leaving no one behind.'

*Table 1 Areas covered by the training package*

| General knowledge | Specific skill |
|---|---|
| Science and technology:<br>- Physical and chemical properties, usage, and environmental behaviours | Analytical skills:<br>- Atmospheric survey and analysis<br>- Solid sample (soil, sediment, and biota) survey and analysis<br>- Water sample survey and analysis<br>- Human biological sample analysis<br>- Methylmercury analysis |
| Regulatory framework:<br>- The Minamata Convention<br>- Standards and guideline values | Management skills:<br>- Quality management<br>- Laboratory safety / environmental management |

This Users' manual provides a sample course with full scope that uses the materials in one consistent programme, but the training package does not need to be used in full. The organizer can prepare the 'custom-made' slide decks from the editable PowerPoint slides of this manual with pre-recorded narration, to fit for its own training programme.

It is recommendable to appoint facilitator(s) to run the sessions of the training programme. The facilitator is not necessarily an expert in mercury monitoring as the technical details are provided by the videos of this training package. Nevertheless, it is recommended that (s)he has sufficient understanding about the context and purpose of the organizing programme.

## <u>Face-to-face or online</u>

The training programme can be organized in face-to-face, online, or hybrid settings. In each case, the facilitator(s) will run the programme and guide the audiences/participants to a certain direction. Online programmes are an emerging training style which has rapidly developed and expended in the past few years. New online platforms and applications have been introduced and become more versatile. However, this approach has some inherent limitation particularly for the topics of mercury monitoring programme. Mercury monitoring is an activity that involves field sampling and laboratory analysis, which are hands-on skills that cannot be completed virtually. Therefore, a hybrid arrangement that combines the video lectures and field/laboratory visits could enhance the understanding and hands-on skills of the participants. This training package includes many videos in the field and the laboratory so that the participant may also exercise the procedures in a face-to-face setting as well. The advantages and limitations of online and face-to-face programme settings are described in Table 2.

*Table 2 Advantages and limitations of online and face-to-face programmes*

| Online programme | Face-to-face programme |
|---|---|
| Logistical arrangement:<br>- Travel arrangements are not required, travel costs are saved.<br>- More people can participate in the programme. | Logistical arrangement:<br>- In the case of local training, most participants live nearby and easily come together.<br>- Field tour, courtesy visit, or other field activities can improve/broaden the understanding of the issue. |
| Time management:<br>- Programme date is flexible. Easy to formulate a series of programmes with certain intervals. (e.g., split into two part and insert intersessional exercise)<br>- Time zone difference should be considered carefully. | Time management:<br>- Full day programmes are possible to intensify the programme with a shorter duration.<br>- More 'active' participation is expected rather than silent listeners. |
| Facility:<br>- Internet connectivity of each participant might be different. Connection cost might be high in some countries.<br>- Applications for online platform such as Webex or Zoom should be installed in computers or other communication devices. The available functions vary in different set up. | Facility:<br>- Meeting venue must be secured for the training programme.<br>- Demonstration of instruments may require dedicated site, room, or facility. |
| Communications:<br>- Difficult to separate from daily work as the participants are physically sitting at their working places. | Communications:<br>- Interactive communication is facilitated. Teambuilding exercise are effective. |
| Recording and reporting:<br>- Due to the virtual nature, confirmation of the attendance of the participants is challenging. | Recording and reporting:<br>- Photos and products of the training programmes are more appealing in the activity report. |

## Multi-country or one country

If the participants of training programme come from multiple countries or regions, time zone difference should be carefully considered. The time zone table indicates the time differences of major cities and possible time setting to cover large geographic areas. Programmes covering wide geographical area are efficient to train many participants at once, but time allocation is smaller as participants staying up to midnight or getting up before dawn may not be well prepared. The time zone table guides the online programme organizers in finding appropriate time arrangement depending on the geographical coverage of the planned programmes. Unless essential, inviting participant from across the entire globe should be avoided. Two out of three time zones, i.e., Africa, Asia and America could be targeted at most. Table 3 indicates possible time slot arrangements in such extreme cases. If the geographical coverage or time difference is smaller, more available time allocation can be found, which is more comfortable to the participants.

*Table 3 Time zone table when organizing multi-country training*

| Location | Africa - Asia | Asia - America | America - Africa |
|---|---|---|---|
| Suva (UTC+12) | 7pm – 10pm | 1pm – 4pm | 4am – 7am |
| Tokyo, Koror (UTC+9) | 4pm – 7pm | 10am – 1pm | 1am – 4am |
| Manila, Kuala Lumpur, Ulaanbaatar (UTC+8) | 3pm – 6pm | 9am – noon | 0am – 3am |
| Bangkok, Jakarta, Hanoi (UTC+7) | 2pm – 5pm | 8am – 11am | 11pm – 2am |
| Yangon (UTC+6:30) | 1:30pm – 4:30pm | 7:30am – 10:30am | 10:30pm – 1:30am |
| Kathmandu (UTC+5:45) | 12:45pm – 3:45pm | 6:45am – 9:45am | 9:45pm – 0:45am |
| New Delhi, Colombo (UTC+530) | 12:30pm – 3:30pm | 6:30am – 9:30am | 9:30pm – 0:30am |
| Male (UTC+5) | Noon – 3pm | 6am – 9am | 9pm – 0am |
| Nairobi (UTC+3) | 10am – 1pm | 4am – 7am | 7pm – 10pm |
| Cape Town (UTC+2) | 9am – noon | 3am – 6am | 6pm – 9pm |
| Vienna, Geneva (UTC+1) | 8am – 11am | 2am – 5am | 5pm – 8pm |
| Sao Paulo (UTC-3) | 4am – 7am | 10pm – 1am | 1pm – 4pm |
| Washington DC (UTC-5) | 2am – 5am | 8pm – 11pm | 11am – 2pm |
| Chicago (UTC-6) | 1am – 4am | 7pm – 10pm | 10am – 1pm |
| Los Angeles (UTC-8) | 11pm – 2am | 5pm – 8pm | 8am – 11am |
| Honolulu (UTC-10) | 9pm – 0am | 3pm – 6pm | 6am – 9am |

The advantage of a one country programme is the use of a local language that significantly enhances the understanding of the participants. Although this training package has been developed in English only, all the scripts of the pre-recorded narration are available as texts, which can be easily translated into local languages. The most technical part of the programme, which is usually delivered by international experts who travels to the programme country, is covered by this training package. The organizers, thus, do not have to find and invite them to provide lectures.

## Invitation, call for participation

Unless the training is planned for internal people only, e.g., staff training, an invitation or call will be developed and distributed to relevant parties. A one-page flyer or a concept note is useful and effective for attracting the attentions of target populations. There are a variety of methods to register the participants. One example is provided for reference.

## Assessment and evaluation

If a training programme is developed as a part of the project activity, the result monitoring is often required. Questionnaire surveys are commonly used for self-assessment on many occasions. Assuming that the programme organizers are not the expert of the issue, this training package provides a sample questionnaire that can serve as pre- and post-training assessment for the participants.

# 3.2 Sample concept note

## Background and Objectives

The Minamata Convention on Mercury (the Convention) is one of the newest multilateral environmental agreements aiming at protecting human health and environment from anthropogenic emissions and release of mercury and mercury compounds. In October 2013, the Convention was formally adopted and opened for signature at a Diplomatic Conference on the Convention convened in Kumamoto, with a ceremonial opening held in Minamata City in Japan.

The Convention entered into force in August 2017 and the Parties to the Convention must abide by the provisions stipulated to the Convention text. There is a growing need for capacity building concerning appropriate mercury monitoring skills in developing countries to ensure the implementation of the required efforts to monitor the levels of mercury and mercury compounds.

The project implemented by [Name of institution] supports participating countries to improve their national mercury-related information base to implement mercury management, especially in the areas of information exchange, awareness and education, research development and monitoring.

The purpose of this training programme is to provide support the enabling efforts for the laboratories that is monitoring (or will monitor) mercury levels in the country. The programme addresses different monitoring needs and priorities of each laboratory by providing methodologies and skills of mercury monitoring in various environmental and biological media.

## Participation Details

**Date:** 01, 02, 03 and 04 July 202X

**Venue:** Virtual meeting, Webex.

**Project title:** [Title of project, if any]

**Training title:** Laboratory management for mercury survey and monitoring

**Participants:** Public laboratories and laboratories in universities that undertake (or will undertake in the near future) mercury analysis for monitoring, survey or research purposes. Laboratories which are able to obtain analytical results by themselves without external resources/supports. No restriction of number of participants from each institution.

**Arrangement:** The training programme is composed of 4 sessions in 4 days, which supports the enabling efforts for the participating laboratories. The topic of the training covers general mercury monitoring and analysis in the environmental and biological media, including several presentations, Q&As, and discussions. Pre- and post-training questionnaire surveys using the online form will be requested to the participants.

**Language:** English only (no interpretation provided)

# 3.3 Sample training course

This is a sample training course that expects extending basic knowledge on mercury science and provides hands on skills to the participants who are involved in mercury analysis. There are many other possible variations and shorter trainings with more focused topics to specific audiences. (The Lecture and Section numbers below refer to the PowerPoint slides of the presentation material in Chapter 5)

**Configuration**

The training course is opened by the organizer with welcome remark and the expectation of the programme towards achieving the expected impact. The programme is divided into four sessions, in which the following topics are addresses:

- Session 1: Atmospheric survey analysis
- Session 2: Solid and liquid sampling and analysis
- Session 3: Human biomonitoring
- Session 4: Advancement to qualified laboratory

Session 1 provides a brief overview of mercury issues and the moves onto atmospheric monitoring techniques using the manual active sampling method. Both field sampling and laboratory analysis are covered in this session.

- Lecture: Properties and environmental behaviour of mercury (extracted from Lecture 1 Sections 1, 2, 6)
- Lecture: Atmospheric survey and analysis Part I (Lecture 2 Part I Sections 1-4)
- Lecture: Atmospheric survey and analysis Part II (Lecture 2 Part II Sections 1-4)

Session 2 explains mercury monitoring for environmental solid and liquid samples such as soil, sediment, biota, and environmental water. Some practical tips and skills are provided for field operators.

- Lecture: Solid sample survey and analysis (Lecture 3 Sections 1-7)
- Lecture: Water sample survey and analysis (Lecture 4 Sections 1-4)

After the explanation lectures, the participants work individually or in groups for assessing the current capacity and challenges of the laboratories where they work. A self-assessment form (Chapter 3.4) is provided for the participants to fill so that they understand the required level of laboratories to produce comparable data. The participants present the finding and assessment results and feedback is given.

Session 3 addresses human biological media, which is another important set of monitoring items. Mercury toxicity can be directly evaluated using human samples such as human hair, which is often collected along with environmental samples. This section explains the analytical process of methylmercury, which is one of the most important indices for assessing mercury risks to humans.

- Lecture: Human biological sample analysis (Lecture 5 Sections 1-3)
- Lecture: Methylmercury analysis (Lecture 6 Sections 1-3)

Session 4 departs from individual monitoring activities and discusses the way towards qualified laboratories that contribute to mercury science and management. The first lecture discusses various monitoring needs in relation to the provisions of the Minamata Convention. Then the next lecture provides a detailed explanation of quality management to ensure the reliability of analytical data. Finally, laboratory safety and environmental management are explained to establish a good laboratory that not only generates qualified data but also takes care of staff and the environment. Finally, follow up plan and actions after the training programme are discussed.

- Lecture: Mercury monitoring and the Minamata Convention (Lecture 7 Sections 1-5)
- Lecture: Quality management (Lecture 8 Sections 1-6)
- Lecture: Laboratory safety / environmental management (Lecture 9 Sections 1-5)

Although the sample course does not provide in-depth discussions on cross-cutting issues on gender and human rights, some reference materials are provided to help the participants understand the importance of this dimension and how it can lead to policy interventions. Adopting an integrated approach on interconnected issues is crucial towards effective policy measures[2].

## Programme agenda

*Day 1*

| Opening session | | |
|---|---|---|
| 00:00-00:05 (5min) | **Get started** – technical set-up, connectivity test, housekeeping | |
| 00:05-00:15 (10min) | **Opening remarks** | Organizer |
| Session 1: Atmospheric sampling analysis | | |
| 00:15-00:25 (10min) | **Introduction**<br>Objectives, expected outcomes and schedule | Organizer |
| 00:25-00:45 (20min) | **Lecture: Property and environmental behaviour of mercury**<br>Physical and chemical properties, mercury products and uses, and environmental behaviours | Video (07’43”) |
| 00:45-00:55 | **Q&A and discussion** | |

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[2] This is in line with the Minamata Convention on Mercury which notes the Parties’ awareness of ‘health concerns, especially in developing countries, resulting from exposure to mercury of vulnerable populations, especially women, children, and, through them, future generations.’ In addition to the health aspects, the Convention further promotes the consideration for the needs of vulnerable populations in health aspects, public information, awareness and education (Article 18), in research, development and monitoring (Article 19), and in effectiveness evaluation (Article 22), are key priorities to be taken forward.

| | | |
|---|---|---|
| (10min) | | |
| 00:55-01:35<br>(40min) | **Lecture: Atmospheric survey and analysis**<br>Manual active sampling method Part I: sample collection | Video (35’01”) |
| 01:35-01:50<br>(15min) | **Q&A and discussion** | |
| 01:50-02:00<br>(10min) | **Break** | |
| 02:00-01:40<br>(40min) | **Lecture: Atmospheric survey and analysis (Continued)**<br>Manual active sampling method Part II: measurement, data processing and QA/QC | Video (26’09”) |
| 01:40-01:55<br>(15min) | **Q&A and discussion** | |
| 02:55-03:00<br>(5min) | **Wrap up**<br>Key points of the day | Organizer |

*Day 2*

| Session 2: Solid and liquid sampling and analysis | | |
|---|---|---|
| 00:00-00:05<br>(5min) | **Get started** – technical set-up, connectivity test, housekeeping | |
| 00:05-00:15<br>(10min) | **Introduction**<br>Introduction of Session 2 | Organizer |
| 00:15-01:05<br>(50min) | **Lecture: Solid sample survey and analysis**<br>Soil, sediment, and biota sample collection and analysis | Video (40’21”) |
| 01:05-01:20<br>(15min) | **Q&A and discussion** | |
| 01:20-01:30<br>(10min) | **Break** | |
| 01:30-02:10<br>(40min) | **Lecture: Water sample survey and analysis**<br>Water sample collection and analysis | Video (28’02”) |
| 02:10-02:25<br>(15min) | **Q&A and discussion** | |
| 02:25-02:55<br>(30min) | **Exercise**<br>Laboratory capacity self-assessment | Facilitator |
| 02:55-03:00<br>(5min) | **Wrap up**<br>Key points of the day | Organizer |

*Day 3*

| Session 2 (continued) | | |
|---|---|---|
| 00:00-00:05<br>(5min) | **Get started** – technical set-up, connectivity test, housekeeping | |
| 00:05-00:45<br>(40min) | **Report back**<br>Results of Exercise by each group including discussion | Facilitator |
| Session 3: Human biomonitoring | | |
| 00:45-00:55<br>(10min) | **Introduction**<br>Introduction of Session 3 | Organizer |
| 00:55-01:25<br>(30min) | **Lecture: Human biological sample analysis**<br>Human biological sample (hair, blood, and urine) analysis | Video (20’10”) |

| | | |
|---|---|---|
| 01:25-01:40<br>(15min) | **Q&A and discussion** | |
| 01:40-01:50<br>(10min) | **Break** | |
| 01:50-02:10<br>(20min) | **Lecture: Methylmercury analysis**<br>Methylmercury analysis, simplified analysis for human hair | Video (11’27”) |
| 02:10-02:25<br>(15min) | **Q&A and discussion** | |
| Session 4: Advancement to qualified laboratory | | |
| 02:25-02:45<br>(20min) | **Lecture: Mercury monitoring and the Minamata Convention**<br>Contribution of mercury monitoring to the Minamata Convention | Video (18’28”) |
| 02:45-02:55<br>(10min) | **Q&A and discussion** | |
| 02:55-03:00<br>(5min) | **Wrap up**<br>Key points of the day | Organizer |

## *Day 4*

| | | |
|---|---|---|
| Session 4 (Continued) | | |
| 00:00-00:05<br>(5min) | **Get started** – technical set-up, connectivity test, housekeeping | |
| 00:05-00:15<br>(10min) | **Introduction**<br>Introduction of Session 4 | Organizer |
| 00:15-01:15<br>(60min) | **Lecture: Quality management**<br>QA and QC, SOP and record, bias and uncertainty | Video (47’22”) |
| 01:15-01:30<br>(15min) | **Q&A and discussion** | |
| 01:30-01:40<br>(10min) | **Break** | |
| 01:40-02:10<br>(30min) | **Lecture: Laboratory safety / environmental management**<br>Safe laboratory operation, environmental management | Video (21’49”) |
| 02:10-02:25<br>(15min) | **Q&A and discussion** | |
| 02:25-02:50<br>(25min) | **Discussions**<br>Towards a qualified laboratory – plan and action | Facilitator |
| 02:50-03:00<br>(10min) | **Wrap up and closing**<br>Way forward | Organizer |

# 3.4 Laboratory capacity self-assessment

In the training programme, the laboratory capacity assessment can be done individually or in groups belonging to the same laboratory. Data collection items can be announced prior to the training so that most of the time can be allocated to the analysis and discussion of the information.

## Basic data

- Name of laboratory
- Organization and Department
- Country

## Self-assessment items

*Sample media and parameters*

Q1: How many sample analyses do you conduct in a year?

| Experience | Media | Parameter | Number of samples per year |
|---|---|---|---|
| Routinely | | | |
| | | | |
| | | | |
| Conducted in the past | | | |
| | | | |
| | | | |
| Future planning | | | |
| | | | |
| | | | |

*Personnel and organization*

Q2: How many staff are there in the laboratory?

Q3: Regarding the staff, how many years of experience in environmental survey/analysis do they have? (Individual information, if possible, otherwise the average for all staff)

Q4: Are there documented or undocumented periodic training programmes for the staff?

*Laboratory workspace*

Q5: Please provide the approximate floor area of the laboratory space for mercury or other heavy metal analysis.

*Methods and procedures for the analysis*

Q6: Which manuals do you follow for sampling and laboratory analysis?

| Media | Parameter | Manual |
|---|---|---|
| | | |
| | | |
| | | |

Q7: Are there documented standard operating procedures (SOPs) for survey / sampling? (if performed)

Q8: Are there documented SOPs for sample preparation?

Q9: Have the records of sampling (if performed) and laboratory analysis been kept?

Q10: Are uniform record formats prepared for sampling (if performed) and laboratory analysis?

*Sample management and storage*

Q11: Is the sample managed using a unique sample code (ID)?

Q12: What are the conditions of sample storage (e.g.: stored in a sample storage room at room temperature, stored in a refrigerator (4 °C), stored in a freezer (-20 °C))?

Q13: Are there documented SOPs for sample management and storage?

Q14: Have the records of sample transportation and storage been kept?

*Laboratory facilities*

Q15: Is the laboratory room controlled for mercury or other trace element analysis? (e.g., the laboratory room is a cleanroom, the room is used only for trace element analysis, the room is used only for water analysis and not for soil, waste, or other high concentration samples, etc.)

Q16: What are the power supply conditions? (e.g., good, sometimes unstable voltage, sometimes blackouts, etc.)

*Laboratory apparatus and reagents*

Q17: How many samples can be analysed in a single operation? (i.e., maximum number that can be treated in a single batch, etc.)

Q18: Which grade of reagents do you use? (e.g., reagent grade, trace element analysis grade, ultra-trace analysis grade, etc.)

Q19: Are there any reagents that are difficult to purchase? (e.g., there is no provider in the country, legal permission is required, etc.)

Q20: What are the storage conditions of the reagents? (e.g., stored in the analysis room, stored in a locked chamber, stored in a refrigerator, etc.)

Q21: Is the usage of reagents managed? (Are date and time of usage recorded?)

Q22: Is the quality of the reagents (e.g., blank amount, interference substances, etc.) checked? (e.g., it is checked before a new provider's product or new production lot is used.)

Q23: Are there SOPs for reagent management?

Q24: Have the records of reagent use been kept? (e.g., date of opening, start and end date of usage, etc.)

Q25: What type of water do you use for analysis? (e.g., distilled water, ion exchanged water, filtered water, combined with these purifications, purchased pure water, etc.)

Q26: Is the measuring equipment (e.g., balance) traceably calibrated to national or international standards?

Q27: How apparatus for analyses are washed and stored? (e.g., washed with ultrasonic, soaked in $HNO_3$ solution during storage, rinsed with deionised water just before use, etc.)

Q28: For QA/QC analysis, is the reference material (RM) or certified reference material (CRM) of a similar material to the sample? (e.g., soil, hair, fish, etc.)

Q29: If yes, which type of RM/CRM? (e.g., product name, media, chemical form, provider, etc.)

*Measuring instruments*

Q30: What instruments do you use for analysis? (Not limited to mercury analysis)

Q31: What is the condition of the instruments? (e.g., good, something malfunctioning, overhaul maintenance has not been carried out for a long time, etc.)

| Type of instrument (e.g., CVAAS, ICP-OES) | Number of Instrument | Condition of instrument |
|---|---|---|
| | | |
| | | |
| | | |

Q32: What is the condition of manufacturer service and supply of parts, and are there difficulties in getting parts supplied? (e.g., good, need a long time to be supplied, etc.)

Q33: What is the status of maintenance service and the estimated downtime when the instruments have mechanical troubles? (e.g., you receive maintenance service from the provider quickly, it takes a long time since there is no technical person (or provider) in the country, etc.)

Q34: Are there SOPs for operation, daily checks and maintenance?

Q35: Have the records of measurements been kept?

*Quality assurance / quality control (QA/QC)*

Q36: What types of QA/QC analysis are performed? (e.g., field blank, operation blank, multiple(duplicate) analysis, instrumental sensitivity check, recovery analysis, CRM analysis)

Q37: Has the limit of detection (LOD) of the analysis in the laboratory been estimated?

Q38: Has the uncertainty of the analysis in the laboratory been estimated?

Q39: Is the Laboratory Information Management System (LIMS) installed?

Q40: Do you periodically participated in international studies or the proficiency tests?

*Environmental management*

Q41: Are there fume hoods/exhaust chambers for toxic exhaust gas?

Q42: Is there gas treatment equipment (e.g., acid gas scrubber, etc.) in the fume hood/exhaust chamber?

Q43: How is wastewater treated? (e.g., treated in the laboratory and drained with municipal water, stored and entrusted to a waste treatment company, treated at a water treatment facility of the facility, treated at wastewater treatment facility of the city, etc.)

Q44: How is the solid waste treated? (e.g., entrusted to a waste treatment company, etc.)

Q45: Has the ISO 14001 certification been accredited?

Q46: Are there documented SOPs for laboratory environmental management? (wastewater/solid waste management, etc.)

Q47: Are there documented SOPs for laboratory safety management?

## Analysis and discussion

- Formulation of medium to long-term future plans for mercury survey and analysis.

- Plans (including procurement plans) for facilities and equipment for analysis.
- Securing and training of personnel.
- Development of a quality management system.
- Participation in interlaboratory comparison (e.g., proficiency testing), information exchange with other institutions, etc.

## 3.5 Pre- and post-training self-test and evaluations

It is important to collect information from the training participants to ensure the participation of target audiences and to assess the effectiveness of the programme. It should be disaggregated by gender and age range when a questionnaire is analysed.

### Full-registration questionnaire

*<Personal information> (all mandatory)*

- First name
- Family name
- Gender (single choice): Male, Female, Prefer not to tell
- Age range (single choice): 19 or below, between 20-29, between 30-39, between 40-49, between 50-59, 60 or above
- Country / Region
- Email

*<Work-related information> (all mandatory)*

- Name of Institution:
- Position in Institution:
- Your role(s) in the institution (Select all that apply to you): Management, administrative work, policy development and implementation, education and lecture, sample/specimen collection and analysis, research planning and experiment, machine operation and maintenances, data processing and analysis, consulting, public relation and communications, student, other (please specify)
- How much of your routine work relates to mercury (single choice): Less than 10%, between 10-50%, more than 50%

*<Baseline survey for progress monitoring>:*

Please respond to these questions based on your own personal knowledge (this is NOT an exam!)

Q1: Have you ever carried out mercury analysis in the following media? (Select all that apply to you).

- Water: ☐drinking water, ☐environmental water, ☐groundwater, ☐wastewater
- Air: ☐ambient air, ☐exhaust gas
- Soil: ☐natural soil, ☐contaminated soil including solid waste, ☐sediment
- Food: ☐fish, ☐shellfish, ☐crops and vegetables, ☐other please specify

- Human: ☐hair, ☐blood, ☐urine, ☐other please specify
- Products: ☐battery, ☐lamp, ☐agricultural chemicals, ☐pharmaceutical products, ☐cosmetics, ☐any other product please specify
- Wildlife: ☐ please specify

Q2: Do you know the differences between elemental mercury and methylmercury in the following areas? (Select all that apply to you).

- ☐Physical property,
- ☐Biological property,
- ☐Toxicity,
- ☐Environmental behaviour,
- ☐Source of generation

Q3: Are you able to explain why mercury is used in the following products and processes?

- Battery: ☐Yes thoroughly, ☐to some extent, ☐not really
- Lamp: ☐Yes thoroughly, ☐to some extent, ☐not really
- Vaccine: ☐Yes thoroughly, ☐to some extent, ☐not really
- Switch: ☐Yes thoroughly, ☐to some extent, ☐not really
- Dental restoration: ☐Yes thoroughly, ☐to some extent, ☐not really
- Thermometer: ☐Yes thoroughly, ☐to some extent, ☐not really
- Sphygmomanometer (manometer): ☐Yes thoroughly, ☐to some extent, ☐not really
- Vacuum pump: ☐Yes thoroughly, ☐to some extent, ☐not really
- Tire balancer: ☐Yes thoroughly, ☐to some extent, ☐not really
- Photographic film and paper: ☐Yes thoroughly, ☐to some extent, ☐not really
- Propellant for satellites: ☐Yes thoroughly, ☐to some extent, ☐not really
- Chlor-alkali production: ☐Yes thoroughly, ☐to some extent, ☐not really
- Vinyl-chloride production: ☐Yes thoroughly, ☐to some extent, ☐not really

Q4: Can you explain the mercury detection theory in cold vapour atomic absorption spectrometry?

- ☐Yes thoroughly, ☐to some extent, ☐not really

Q5: Can you properly select and design the monitoring methodology for the following surveys?

- Mining site: ☐Yes thoroughly, ☐to some extent, ☐not really
- Waste-dumping site: ☐Yes thoroughly, ☐to some extent, ☐not really
- Vulnerable population: ☐Yes thoroughly, ☐to some extent, ☐not really

Q6: Can you differentiate the blood, urine and hair testing for assessing human health risks due to mercury exposure?

- ☐Yes thoroughly, ☐to some extent, ☐not really

**Post-training evaluation questionnaire**

Each answer should be linked with the registration information so that the personal attributes can be used for statistical analysis.

*<Personal information> (all mandatory)*

- First name
- Family name
- Country / Region
- Email

*< About the training programme >*

Q1: Could you rate the overall level of the presentations that you received in comparison with your personal competency?

- ☐Too high, ☐slightly high, ☐just fit to me, ☐slightly low, ☐too low

Q2: Could you select one presentation/topic that interests you the most? (Single choice)

(List all presentations or topic here)

Q3: Who do you think was the most suitable people/section in your institution to participate in this training programme? (Select all that apply to you).

- ☐Myself, ☐my co-workers, ☐ specific section of the institution (please specify), ☐no one in my institution

Q4: What will you do with the information received in this training programme? (Select all that apply to you).

- ☐Apply it to my daily work, ☐share it to my colleagues and others, ☐ask UNEP for more/specific information, ☐ other (please specify), ☐none at this moment

## Post-training evaluation for progress monitoring

These questions are asked to measure the contribution of the training programme for developing capacity. The numbers are respective to the baseline survey for progress monitoring done prior to the training.

Q2: Do you think the programme helped to improve your understanding on the difference between elemental mercury and methylmercury in the following areas? (Select all that apply to you).

- ☐Physical property,
- ☐Biological property,
- ☐Toxicity,
- ☐Environmental behaviour,
- ☐Source of generation

Q3: Do you think the programme helped your understanding why mercury is used in the following products and processes?

- Battery: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Lamp: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Vaccine: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Switch: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Dental restoration: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Thermometer: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Sphygmomanometer (manometer): ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Vacuum pump: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Tire balancer: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Photographic film and paper: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Propellant for satellites: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Chlor-alkali production: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme

- Vinyl-chloride production: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme

Q4: Do you think the programme helped you to understand the mercury detection theory in cold vapour atomic absorption spectrometry?

- ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme

Q5: Do you think the programme helped you to be able to properly select and design the monitoring methodology for the following surveys?

- Mining site: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Waste dumping site: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme
- Vulnerable population: ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme

Q6: Do you think the programme helped you to differentiate the blood, urine and hair testing for assessing human health risks due to mercury exposure?

- ☐ Helped a lot, ☐helped to some extent, ☐no difference, ☐more confusing to me, ☐ the item was not relevant in this programme

# 3.6 Frequently Asked Questions

In the course of the training programme, participants will ask questions to deepen their understanding. Some responses made by the lecturers about this lecture materials in the past training programmes are compiled here for future reference. Similar questions can be addressed in the same way so that the messages conveyed to the participants will be consistent.

### Laboratory management

| Question | Answer |
|---|---|
| 1. What are the major risks and opportunities of a mercury testing laboratory? | One opportunity for the laboratory is the high value of the data. High quality data can lead to find new facts. On the other hand, a risk can be the misinterpretations of the surveys/experiments due to low quality data. |
| 2. Could you please specify the primary treatment for laboratory wastewater contaminated with mercury? | Activated carbon can be used as a way to remove mercury from wastewater. However, since the efficiency and characteristics of treatment methods differ depending on factors such as the properties of the wastewater and coexisting substances, the treatment method must be thoroughly examined in advance. |
| 3. Why is it not necessary to have ISO 14001 accreditation? Is the audit not necessary? | Official ISO 14001 certification with audit is effective since it confirms defects that are not noticed by the laboratory itself. But it is costly. Even if there is no official certification, operating an environmental management system with reference to the requirements of ISO 14001 is very effective for environmental management during the accreditation period. The benefit of ISO 14001 management system without certification is also described in the ISO publication. |

## Quality control and assurance

| Question | Answer |
|---|---|
| 1. For testing laboratory, is ISO/IEC 17025 best standard rather than 14001? | ISO/IEC 17025 is focused on procedures for the quality management systems for testing laboratories. However, testing laboratories should also be managed under environmental management, thus ISO 14000 standards are helpful for the environmental management of laboratories. |
| 2. How often do reagent blanks need to be performed? | A reagent blank should be confirmed prior to the first usage of the reagent. When the type of reagent (such as provider, or grade) is changed, its blank should be confirmed again. Even if an operation blank is analysed on every analysis, periodical tests of reagent are recommended. When a large operation blank is found, each reagent used in the analysis should be checked to find the source of the blank. |
| 3. Can the samples for interlaboratory comparison be used as control samples for the laboratory analysis? | Yes, remaining interlaboratory testing samples are also good reference materials for QA/QC. |
| 4. What do 3s and 10s mean for limit of detection, LOD, and limit of quantification, LOQ? | Assuming the probability of the analysis is following normal distribution, 99.7% of the results are expected to fall within the 3s range. When 3s is defined as the LOD, it is the level that the analysis results are deemed appropriate (i.e., a difference can be clearly shown). Of course, in this case, it is necessary to separately verify that the measuring device can reliably detect the numerical value of 3s (the signal can be separated from the background). As for the LOQ, the meaning of 10s cannot not be clearly explained, but it is one way to consider that 10s is sufficient level to treat the analytical results statistically. The LOD/LOQ of 3s and 10s is described in some manuals (not limited to the Japanese manual for the mercury analysis). One of the advantages is that it can be easily calculated. |
| 5. In reporting, which is better, the standard error of the mean or simply the standard deviation? | Basically, the test instructions must be followed. The standard deviation of the results represents the uncertainty in each analysis, while the standard error of the mean represents the uncertainty of the reporting value (mean), so they have different meaning. |
| 6. Please explain in detail rectangular and triangular distributions. | Triangular and rectangular distributions are used for uncertainty estimation of the type B approach. For estimations of type A, the uncertainty is estimated from the standard deviation of the multiple experiment of the measurement. In many cases of the type B analysis, the actual uncertainty is unknown (e.g., the pipette, which is assigned, is the only guaranteed value, not an uncertainty). In such cases, the probability distribution of the value to estimate the uncertainty should be assumed. If the probability distribution of the values is expected to be similar to the normal distribution, a triangular distribution is considered to represent the actual distribution. If the values are considered to be distributed almost evenly within the guaranteed values, a rectangular distribution is more suitable. |

## Survey plan and sampling

| Question | Answer |
|---|---|
| Air monitoring | |
| 1. What is the JIS code for an air monitoring method? | The manual is published by the Japanese government, but it is not in the JIS series. |
| 2. Is the sampling method traceable to other official standards like ISO? | The sampling method explained in the lecture is from the manual of the Japanese method, which does not fall under or related to the ISO method. It is not possible to make a reference for data validation with this method, but it is a well-established methodology reviewed thoroughly by the technical committee during the preparation process. A draft English translation of the manual of the Japanese method is available on the website of the Minamata Convention. (MOEJ (2004). Mercury analysis manual, March 2004.). |
| 3. What is the detection limit of this manual method? | It depends on the measuring instrument, but in the condition of the lecture (0.5 L/min and 24-hour sampling, CVAAS measurement), the LOD is usually lower than 0.1 ng/m$^3$. This LOD is much lower than the atmospheric mercury concentration in the background area. |
| 4. Is the toolbox shown standard, or an equivalent device can be used? | The device in the toolbox is not a standard, and can be built from the individual devices (e.g., pumps, tubing, and thermometer) available on the market. Other types of devices such as pumps having sufficient performance is available. |
| 5. The method of the USEPA (chapter IO-5) uses 2 gold cartridges. What is the difference between using 1 trap and 2 traps? | The second gold cartridge described in the USEPA method IO-5 is used to confirm the break-through of mercury from the first cartridge. Basically, the procedures of this lecture's method (based on the Japanese manual) and the IO-5 method are the same. |
| 6. For a duplicate or triplicate sampling, does each tube have its own pump? How do you troubleshoot the problems with pump? | When multiple gold cartridges are connected to the same pump, not all cartridges have the same flow rate. Thus, one pump is necessary for each gold cartridge. In the case of pump malfunction, pumps are normally replaced or fixed by the manufacturers. |
| 7. How is the gold amalgamation cartridge cleaned? Are there any kits or products available in the market? | There are no products only for cleaning the gold amalgamation cartridge sold in the market. However, mercury collected in the gold amalgamation cartridge is purged out during the measurement. Therefore, the gold cartridge is simply cleaned by measuring it. To confirm whether the gold amalgamation cartridge is well cleaned, the gold cartridge can be used for measurement once more (this measurement can work as a re-clean-up of the gold cartridge). |
| 8. What type of tubing can be used? | During sampling, tubing is used downstream of the gold cartridge, so that tubing has little effect on sample collection. Therefore, many types of tubing can be used as long as they are clean and have no leakage. |
| 9. What is the requirement of soda lime in the sampler inlet? Does it interfere with the mercury concentration? | The soda lime is composed of lime and some alkali such as sodium hydroxide. The soda lime absorbs the gaseous oxidized mercury (GOM) in the air. However, since the atmospheric GOM concentration in ambient air is so small, it has little effect on the total concentration of atmospheric mercury. Soda lime has no other effect on the sampling and measurement of mercury in the atmosphere. The detailed process of removing the interfering substances is still unknown, but the interfering gaseous substances such as SOx, NOx are effectively absorbed by the alkaline in soda lime. |

| Question | Answer |
|---|---|
| 10. What brand/purity of soda lime is recommended? How is it cleaned? | The ideal soda lime composition is still under research, but many of soda limes which are commercially available can be used. However, it is necessary to check the mercury blank before the first use. If a blank is detected, the blank can be reduced by heating the soda lime at a high temperature (about 250 °C). |
| 11. Please provide more details regarding the particle filter. | In this lecture, a membrane filter with 0.45 micrometre pore size is used. However, to remove the serious interference of particle matter in the air, several types of filters which do not contain mercury, and do not absorb atmospheric mercury can be used. |
| 12. Is there any specific periodic flow rate during the 24-hour monitoring? | There is no specific flow rate. However, the Japanese manual requires 0.1-0.5 L/min of flow rate for 24-hours sampling. To avoid deviation from the diurnal variations at the survey site, 24-hours sampling is recommended to obtain the general situation of the site. |
| 13. What is the relationship between the flow rate and mercury sampling at 0.5 L? | In most cases, there is a linear relationship in the range from around 0.1 L/min to 1 L/min. The sampling amount should be changed when the concentration is expected to vary. In such cases, the sampling amount can be changed with the flow rate of above range or sampling duration. |
| 14. In case of high Hg concentration, can we reduce sampling time or flow rate? For example, can we reduce to the duration to 4 hours? How much concentration can be considered as high? | In general cases, the LOD of the method is lower than 0.1 ng/m$^3$ for 24-hour sampling. In most of the general background situations, atmospheric mercury concentration is around 1 ng/m$^3$ (in southern hemisphere, there are cases where the concentration is somewhat lower). Thus, 3 hours or more sampling can be done when the mercury concentration is larger than the LOD. However, the relative uncertainty of the results usually becomes larger when the amount (not concentration) of mercury is very small. The calibration standard of the measurement should cover the expected mercury amount range. Also, when the sampling duration is decreased to shorter than 24 hours, it should be noted that the data may be affected by the diurnal variation of the concentration. |
| 15. How the sampling volume can be changed by flow rate or any other means? | Sampling flow volume can be changed to suit the objective and situations of the survey. For example, sampling in the high atmospheric mercury concentration areas, a smaller sample volume is sufficient to analyse the concentration. Sampling volume can be changed both by changing flow rate and sampling duration. The Japanese manual prescribes the flow rate to be between 0.1 - 0.5 L/min. With a very small flow rate, it becomes difficult to measure the accurate flow volume. On the other hand, with very large flow rate (such as over the 1.0 L/min), the mercury collection rate by a gold cartridge may be low. |
| Solid monitoring | |
| 16. Is there any potential risk of bias when using metal tools during field sampling? | Strictly speaking, metal sampling tool may affect the mercury concentration of the sample. However, considering the concentration level of the soil/sediment samples and the areas of contact between the tools and samples, the effect of metal (steel) tools for solid sample is usually small. Nevertheless, those metals, which create amalgam with mercury, such as copper or aluminium, should be avoided. For the water samples, because of its low concentrations, metal tools should be avoided. |

| Question | Answer |
|---|---|
| 17. Are there any differences in the distribution of methylmercury depending on the fish species? | The distribution tendency of methylmercury in the organs does not differ greatly between different species. But there may be a slight difference in some species due to their metabolic systems. |
| 18. How can we assure the representativeness of muscles sampling? | In general, there is not much difference in mercury in the muscle tissue of same organism, but some concentration differences from site to site. It is recommended to homogenize the entire muscle of the sample to ensure sufficient homogeneity. |
| Water monitoring | |
| 19. Are there any other methodology for long-time storage of water samples? Is it sufficient to add HCl? | (Inorganic) mercury in water is rather unstable and easily volatilized. Freezing is a good method for long-time storage, but it may not be easy to use freezers to keep many water samples since water samples are usually bulky. Stabilisation with bromine monochloride (BrCl) is effective to stabilise mercury in water. In many cases, BrCl added (usually about 0.5 %) water samples can be stored for a month or more. However, BrCl is a hazardous reagent and should not be used at the sampling sites. To stabilise water samples with BrCl, the samples are brought back to the laboratory before adding BrCl. |
| Biomonitoring | |
| 20. If we make a study about the effect of mercury on people and their habits, which sample is better, hair, nail or urine? | Sampling should be selected in consideration of the objective of the survey. If the most important exposure of the subject people is expected to be methylmercury from the food, hair is a good sample. To obtain the information of elemental (gaseous mercury) or inorganic mercury exposure, urine is a good sample. Nail is also a good indicator for methylmercury exposure although only few research reports are available. The nail samples have advantages such as less customary resistance of the participant to sampling and relatively less external influence than hair (mercury concentration in hair may be affected by breaching, permanent waves, personal care products, etc.). |
| 21. Normally what is the ratio of inorganic mercury to methylmercury in the human body? Which type of mercury (inorganic or methyl) is more toxic? | Except the people who are living in the area of high concentration of atmospheric mercury (such as ASGM), most mercury exposure is methylmercury from food, and most mercury in the bodies of general population is methylmercury. In terms of the biological half-life and toxicity, methylmercury is more serious than inorganic mercury. However, gaseous elemental mercury (GEM) is inhaled from the lungs, and a high concentration of GEM seriously affects the nervous systems. Therefore, a very high concentration of GEM is also very toxic, although such situation hardly occurs except for rare occasions such as the situation described above. Methylmercury in the human body is excreted in faeces, Also, some methylmercury is accumulated in hair or changed into inorganic mercury and excreted to urine. |

| Question | Answer |
|---|---|
| 22. What can be expected from the result of total mercury analysis of the human hair? Can the results provide information on exposure to elemental or inorganic mercury? | Almost all mercury in hair is methylmercury as a result of the metabolism in the body. Although very little elemental and inorganic mercury accumulates in hair, when the subject person is exposed a high amount of elemental or inorganic mercury (e.g., under the high gaseous mercury environment, using mercury added personal care product), elemental or inorganic mercury may adhere to the surface of hair. Even though a quantitative evaluation is difficult, information of exposure of such elemental or inorganic mercury can be obtained from total mercury analysis. However, to distinguish the methylmercury exposure, methylmercury analysis of hair sample is required in addition to total mercury analysis. |
| 23. Should the subject person refrain from dying the hair? | In practice, it may be difficult to restrict the activity of the subject person, but hair treatments affect the mercury concentration in hair (bleaching and permanent waves treatment have a relatively large effects). Adding information about these hair treatments to the questionnaire for the subject person is valuable when analysing the results. |
| 24. Is there any effect on the mercury concentration if metal scissors are used for hair sampling? | If only mercury is to be analysed, the use of metal scissors has virtually no effect on the sample. However, they should be washed and dried well before use. |
| 25. What percentage of total mercury is methylmercury? | Methylmercury predominates in living organisms due to biomagnification and the difference in half-life in the bodies. Most mercury in the muscle tissues of living organisms is thought to be methylmercury, but several reports have found considerable amounts of inorganic mercury. Most mercury accumulated by metabolism in human hair is methylmercury, but elemental mercury and inorganic mercury can adhere to the surface of hair due to the influence of the participant's living environment or the use of mercury-added product. |
| 26. How can the results of total mercury and methylmercury be compared? Is there any commonly known large difference in concentration? | Methylmercury is especially toxic compared to other chemical forms of mercury (except dimethylmercury, but its concentration in the environment is very low). Therefore, the actual concentration of methylmercury provides very important information. The objective of methylmercury analysis is to correctly analyse the exposure status and the toxicity as the human food. For biota samples, most mercury in the muscle tissues is methylmercury. However, some reports have found considerable amounts of inorganic mercury in the muscle tissues. The organs such as the liver may have some amount of inorganic mercury. |

## Analytical processes

| Question | Answer |
|---|---|
| Methodology | |
| 1. Is it possible to measure total mercury in hair sample by CVAAS? | Yes, hair sample can be measured by methods such as acid digestion-CVAAS or thermal decomposition CVAAS. Although the amounts of hair samples are small, sufficient data can be obtained since the concentrations of mercury in hair are higher than those in other human organ samples such as blood. |
| 2. On the measurement of reduction aeration CVAAS, must the mercury vapour from the reaction chamber is purged into the absorption cell of the CVAAS assembly be dried or not? | Too much moisture should be avoided to be introduced into the measurement cell, however, the measurement gas purged from the reaction vessel does not need to be completely dried. The instrument used in this lecture traps moisture with the cold trap. |
| 3. Which concentrations are usually reported for soil and sediment samples, wet-based or dry-based? | It depends on the objective of the survey. For example, the provisional removal standard of the sediment in the Japanese legislation is dry-based. |
| Reagent and gas | |
| 4. For the sample preparation by acid digestion, can other oxidizing agents be used to complete oxidation in addition to the prescribed acid solutions? | Even though most soil, sediment or biota samples can be easily digested by reagents such as nitric acid, hydrochloric acid and sulphuric acid as mentioned in the lecture, other oxidizing agents can be used. However, the following items should be kept in mind: 1) there are cases where mercury in the digested solution volatizes even in the presence of oxidizing agents. 2) The reagents having high oxidization voltages prevent reduction during the measurement. |
| 5. For the reduction aeration CVAAS measurement, is it preferable to use 0.1 % sodium borohydride instead of stannous chloride? | Yes, sodium borohydride can be used to create mercury hydride. Some types of the CVAAS instruments in the market uses this hydride generation system. |
| 6. For the gold amalgamation trap measurement, can the mercury standard solution be used for calibration instead of the standard mercury gas? | The standard solutions can be used to calibrate for the atmospheric mercury measurements using a closed apparatus and a reducing agent such as stannous chloride. Further explanations are provided in the lecture materials. |
| 7. For the gold amalgamation trap measurement, can we use other inert gases instead of air pump to carry mercury vapour into the AAS instrument? | Yes, alternative inert gases such as nitrogen gas or air may be used if they contain no traces of mercury. Mercury free air is probably the cheapest option. However, if the flow rate of the gas is changed during the measurement operation, the mechanics of the measuring device may be complicated. |
| 8. For the reduction aeration CVAAS measurement, can other inert gases such as argon be used as a carrier gas instead of air? | Although argon gas or other inert gases can be used, they are not easy to use in the CVAAS instrument explained in this lecture because there is a process of closed circulation. |
| Preparation | |
| 9. Before the hair is cut into small pieces, must it be cut approximately 3 cm from the base of hair? | Collected hair samples should be cut to a length that fits the objective of the survey before mercury analysis. Since human hair generally grows about 1 cm per month, cutting 3 cm from the root allows the evaluation of the exposure environment of the subject person for the past 3 months. |

| Question | Answer |
|---|---|
| 10. How can the urine samples be analysed to obtain accurate result? | In some cases, the analytical result of urine samples may have lower accuracy. As mercury in urine samples (mostly oxidized mercury) is easily volatized, stabilization of mercury during storage and analysis is important. Urine samples should be frozen before analysis. If it is not possible, analysis should be conducted immediately after sample collection. |
| 11. Apart from hair samples, how should other biota samples such as fish muscles be dried, in an oven or freeze dried? | This method can be used for normal wet samples such as fish muscle tissues. However, the samples with very high moisture content may require moisture removal. Freeze-drying is a good method in terms of stability of methylmercury in the samples and sample handling during analysis. It is possible to dry in an oven, but the drying conditions such as temperature and time should be considered. |
| Methylmercury analysis | |
| 12. It is a long procedure. What is the recovery rate? | Although it is a long procedure, the recovery of mercury using this method becomes quite steady and almost 100% recovery of methylmercury is possible. |
| 13. Are there any quick qualitative methods for methylmercury in biological samples? | There are some other methods for methylmercury analysis. Also, some research reports suggest simpler analysis methods. Such methods can be used, but the key features of such methods (e.g., data uncertainty, interfering substances on analysis, LOD) should be carefully considered to confirm that the objective of the survey can be fully met. |
| 14. Is the concentration process required before injection into the GC instrument? | In this method, sample solution is prepared in a volume of (usually) 0.5 mL by liquid-liquid extraction. No additional concentration procedure is needed. |
| 15. Can the polypropylene centrifuge tubes be used for the dithizone-extraction GC/ECD method? | From the viewpoint of the methylmercury blank, polypropylene usually has little effect. However, it is recommended to avoid polypropylene tubes for dithizone extraction method, because toluene may dissolve the interfering organic substances from the tube. |
| 16. What kind of column is used? | In the method explained in the lecture, a packed GC column is used. Following the description of three types of GC columns in “Mercury Analysis Manual”, either type of columns can be used for the analysis:<br>- 3.0 mm × 0.75-1.0 m glass column packed with Hg-20A on Uniport HP (AW-DMCS, 60-80 mesh, GL Science Co., Ltd., Tokyo, Japan).<br>- 3.0 mm × 0.75-1.0 m glass column packed with 10 % KOCL-Hg on Chromosorb W (AW-DMCS, 60-80 mesh, J-Science Co., Ltd., Kyoto, Japan).<br>- 3.0 mm × 2.0 m glass column packed with 5-10 % poly-diethylene glycol succinate (DEGS) on Chromosorb W (AW-DMCS).<br>After packing the column, approximately 2-3 cm of NaCl, previously heated at 500 °C for 2-3 hours, in packed on top of the packing material (at the injection port). |
| 17. Are the reagent grade solvents sufficient? Does it need to have a GC grade? | Although precise comparisons have not yet been carried out, many reagent grade solvents are available. However, checking the reagent blank is necessary before using for the first time (it must be done either for the reagent grade or GC grade). |

| Question | Answer |
|---|---|
| 18. Is the analytical method done parallel with the standards? What are the forms of standards? | Yes. In this method, the analytical procedures are also performed for the standard solutions for calibration curve (from sample preparation to GC/ECD measurement). Prepared methylmercury solutions or standard solutions on the market can be used, as well as the CRM of methylmercury that has similar characteristics to the samples are applicable. |
| XRF analysis | |
| 19. Can the XRF be used for the direct soil sampling during the screening process? | Yes, XRF can measure the samples directly, hence XRF can be used for direct measurements of unprepared samples. However, mercury added products such as batteries need to be disassembled so that the particular parts can be measured, as mercury is intentionally added. |
| 20. Dental amalgam generally contains about 40-50 % of mercury. Can it be measured using XRF? | Yes, XRF is a good method to measure dental amalgam. As most of other analysis methods are focused on much lower mercury concentrations than that of dental amalgam, a dilution with a large ratio is necessary during the sample preparation. However, it should be noted that the measurement results by XRF have a relatively large uncertainty due to the difference in the characteristics of the sample. |
| 21. How can dental amalgam samples be digested? | Since dental amalgam is composed of a mixture of silver, tin, zinc, copper, and mercury, it is easily digested by oxidizing acids. However, most analysis methods for mercury using CVAAS are focused to measure mercury concentration in the nanogram orders. While approximately a half of dental amalgam is mercury, a ridiculously small amount of dental amalgam must be used, or very large ratio of dilution is necessary, if the CVAAS method is used. For the analysis of dental amalgam, other methods such as XRF may be more suitable. |

# 4 SUPPLEMENTARY INFORMATION AND LITERATURE

Background and in-depth information are compiled in this chapter. The users can refer, as necessary, to the material to add value to their own training programme. Some information is slightly beyond the scope of this training package, but it will serve as a guidance for extended self-study.

## 4.1 Outlines of the Minamata Convention on Mercury

The Minamata Convention on Mercury is a multilateral legally-binding environmental agreement aiming to protect the human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds. The text was adopted in October 2013, and is composed of a preambular text, 35 articles, and 5 annexes. The Convention entered into force on 16th August 2017, on the 90th day after the deposition of the 50th instrument of ratifications, acceptance, approval, or accession.

In its preamble, the Convention recognises the substantial lessons of Minamata disease, in particular the serious health and effects resulting from the mercury pollution, and makes aware of the health concerns to women, children, and future generation. The Convention sets out a range of measures throughout the entire lifecycle of mercury to meet its objective, which include measures to control the supply and trade of mercury, and to control mercury-added products and manufacturing processes in which mercury or mercury compounds are used, as well as artisanal and small-scale gold mining. The text also includes the articles on emissions and releases of mercury, on environmentally sound interim storage, on mercury waste, and contaminated sites.

Articles 3 – 12 relate to the operational provisions describing Parties' obligations to reduce emissions and releases, with controls along their life cycle. Articles 13 – 21 facilitate the implementation of these measures including provisions related to support to the Parties, information and awareness raising and reporting. Articles 22 – 35 cover the overall management of the Convention. It is also worth noting that the Convention promotes consideration of the needs of vulnerable populations in health aspects; in public information, awareness and education; in research, development and monitoring; and in effectiveness evaluation; are key priorities to be taken forward. Annexes A and B list the mercury-added products and manufacturing processes to be controlled by the Convention. Annex C sets the items to be included in the national action plans for artisanal and small-scale gold mining (ASGM). Annex D lists the point source categories for emission control.

*Table 4 Article-by-article outlines of the Minamata Convention*

| Article | Outlines |
|---|---|
| Preamble | Recognition of mercury risks, substantial lessons of Minamata Disease |
| Article 1 Objective | Protection of the human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds. |
| Article 2 Definitions | Definition of terms in the Convention. |
| Article 3 Supply and trade | Control of primary mercury mining by setting the phase out period.<br>Prohibition of international trade of mercury except for the use allowed under the Convention. |
| Article 4 Mercury-added products | Control (including phase out and phase down) of production, import and export of the mercury-added products in Annex A. |
| Article 5 Manufacturing processes | Control (including phase out) of mercury uses in the processes specified in Annex B. |
| Article 6 Exemptions | Registration of exemption from the phase out dates specified in Annexes A and B. |
| Article 7 ASGM | Reduction (or elimination wherever feasible) of mercury use in ASGM for the countries having more than insignificant ASGM activities. Development and implementation of national action plans in accordance with Annex C. |
| Article 8 Emissions | Control of emission into air from the source categories listed in Annex D based on the best available techniques and best environmental practices. Preparation of inventory. |
| Article 9 Releases | Identification of relevant source categories that are not addressed in other provision of the Convention. Control of releases to land or water. Preparation of inventory. |
| Article 10 Interim storage | Environmentally sound interim storage of mercury other than waste mercury. |
| Article 11 Mercury wastes | Management of mercury wastes in an environmentally sound manner, taking into account the guidelines developed by the Basel Convention. |
| Article 12 Contaminated sites | Identification and assessment of sites contaminated by mercury or mercury compounds. |
| Articles 13 – 14 Finance, technical assistance | Financial resources and mechanisms, capacity-building, technical assistance and technology transfer. |
| Article 15 Compliance | Establishment of a Committee as a subsidiary body of the COP, to promote implementation and review of compliance. |
| Article 16 Health | Development and implementation of the health strategies and programmes to protect population at risk. Development of science-based educational and preventive programmes on occupational exposures. Appropriate health-care services for affected populations. Strengthening capacity for diagnosis, treatment and monitoring of health risks. |
| Articles 17 – 18 Information, awareness, education | Exchange of scientific, technical, economic and legal information among the Parties. Promotion and facilitation of the provision of information to the public. |
| Article 19 Research, monitoring | Cooperation for research and development on inventories, modelling and monitoring, impacts on human health and the environment, fate and transport, commerce and trade, mercury-free alternatives, etc. |

| Article | Outlines |
|---|---|
| Article 20 Implementation plans | Development and execution of implementation plans taking into account the domestic circumstances. |
| Article 21 Reporting | Periodical reporting to the COP on measures taken by the Parties. |
| Article 22 Effectiveness evaluation | Evaluation of the effectiveness of the Convention on the basis of available scientific, environmental, technical, financial and economic information. |
| Articles 23 – 28 COP, Secretariat, etc. | The COP, secretariat, settlement of disputes, amendments, voting. |
| Articles 29 – 35 Ratification, etc. | Signature, ratification, entry into force, reservation, withdrawal, depositary, and authentic texts. |
| Annex A Mercury-added products | Introductory text: General exceptions.<br>Products essential for civil protection and military uses<br>Products for research, calibration of instrumentation, for use as reference standard<br>Where no feasible mercury-free alternative for replacement is available<br>Products used in traditional or religious practices<br>Vaccines containing thiomersal as preservatives<br>Part I: Products to be phased out<br>Batteries; switches and relays; lamps; cosmetics; pesticides, biocides and topical antiseptics; non-electronic measuring devices<br>Part II: Dental amalgams. |
| Annex B Manufacturing processes | Part I: Chlor-alkali production, acetaldehyde production.<br>Part II: Vinyl chloride monomer, sodium or potassium methylate or ethylate, polyurethane. |
| Annex C ASGM national action plans | Content of national action plan. |
| Annex D Point sources of emissions | Coal-fired power plants; coal-fired industrial boilers; smelting and roasting processes used in the production of non-ferrous metals; waste incineration facilities; cement clinker production facilities. |
| Annex E Arbitration | Arbitration and conciliation procedures. |

Source: Minamata Convention (2013). Text of the Minamata Convention on Mercury for adoption by the Conference of Plenipotentiaries.

## 4.2 Standards and guideline values

The monitoring results are compared with some other values for judging if the analysed values are above or below such values. For compliance monitoring, the standards and guideline values set by the authorities are used for such comparison. For research monitoring, similar monitoring results at the control sites are often used. The comparison values should be carefully chosen to avoid misleading the issue. For example, the guideline values for methylmercury toxicity should not be used for assessing elemental mercury exposures. The interpretation of the results should also be aligned with the conditions used by the particular guidelines. The tables below are not exhaustive lists but indicate a few examples of values which are frequently referred to. For the actual monitoring activity, the local standards and guidelines should always be checked.

*Table 5 Air (mercury standards and guideline values)*

| Issued | Target | Parameter | Type | Value | |
|---|---|---|---|---|---|
| WHO Europe[1] | Indoor air | Total mercury | Guideline value | 1 µg/m$^3$ | Annual mean |
| WHO[2] | Indoor air | Total mercury | Guideline value | 0.2 µg/m$^3$ | Estimated tolerable concentration for long-term exposure |
| ILO[3] | Workplace | Aryl mercury | Guidance note | 0.1 mg/m$^3$ | 8-hour time-weighted average |
| | | Elemental and inorganic mercury | | 0.025 mg/m$^3$ | |
| | | Organometallic alkyl mercury | | 0.01 mg/m$^3$ | |
| MOEJ[4] | Ambient air | Total gaseous mercury | Guideline value | 40 ng/m$^3$ | Annual mean |
| MOHLWJ[5] | Working environment | Inorganic mercury | Administrative level | 0.025 mg/m$^3$ | |
| | | Alkyl mercury (methyl and ethyl only) | | 0.01 mg/m$^3$ | |

Source: 1 World Health Organization WHO (2000). 2 WHO (2021). 3 Niu *et al.* (eds.) (2022)., 4 Japan, Inter-Ministerial Coordination Council on the Minamata Convention on Mercury (2017). 5 Japan, Ministry of Labour (1988).

*Table 6 Water (mercury standards and guideline values)*

| Issued | Target | Parameter | Type | Value | |
|---|---|---|---|---|---|
| WHO[1] | Drinking water | Total mercury | Guideline value | 1 μg/L | |
| USEPA | Freshwater | Inorganic mercury | Criterion maximum concentration | 1.4 μg/L | National Recommended Aquatic Life Criteria[2] |
| | | | Criterion continuous concentration | 0.77 μg/L | |
| | Saltwater | | Criterion maximum concentration | 1.8 μg/L | |
| | | | Criterion continuous concentration | 0.94 μg/L | |
| | Drinking water | | Maximum contaminant level goal | 0.002 mg/L | National Primary Drinking Water Regulation[3] |
| | | | Maximum contaminant level | 0.002 mg/L | |
| EU[4] | Inland surface water | Mercury and its compounds | Environmental quality standard | 0.07 μg/L (dissolved) | Maximum allowable concentration |
| | Other surface water | | Environmental quality standard | 0.07 μg/L (dissolved) | |
| | Biota | | Environmental quality standard | 20 μg/kg (ww) | |
| MOEJ[5] | Public water (river, lake, sea) | Total mercury | Environmental quality standard | 0.0005 mg/L | |
| | | Alkyl mercury | Environmental quality standard | Not detectable (0.0005 mg/L) | |
| | Groundwater | Total mercury | Environmental quality standard | 0.0005 mg/L | |
| | | Alkyl mercury | Environmental quality standard | Not detectable (0.0005 mg/L) | |
| | Wastewater | Total mercury | Wastewater quality standard | 0.005 mg/L | |
| MOHLWJ[6] | Tap water | Total mercury | Drinking water quality standard | 0.0005 mg/L | |

Source: 1 WHO (2021). 2 United States of America, Environmental Protection Agency USEPA (2022a). 3 USEPA (2009). 4 European Union EU (2013). 5 Japan, Inter-Ministerial Coordination Council on the Minamata Convention on Mercury (2017). 6 Japan, Ministry of Health, Labour and Welfare MOHLWJ (2020)

*Table 7 Soil (mercury standards and guideline values)*

| Issued | Target | Parameter | Type | Value |
|---|---|---|---|---|
| MOEJ[1] | Soil (leaching test) | Total mercury | Environmental quality standard | 0.0005 mg/L |
| | | Alkyl mercury | | Not detectable (0.0005 mg/L) |
| | | Total mercury | Soil contamination countermeasure standard | 0.0005 mg/L (0.0005 mg/L) |
| | | Alkyl mercury | | Not detectable |
| | Soil (content) | Total mercury | | 15 mg/kg |

Source: 1 Japan, Inter-Ministerial Coordination Council on the Minamata Convention on Mercury (2017).

*Table 8 Sediment (mercury standards and guideline values)*

| Issued | Target | Parameter | Type | Value |
|---|---|---|---|---|
| MOEJ[1] | Sea sediment | Total mercury | Interim Standards for Sediment Removal | Removal standard (mg/kg (dw) or ppm) *<br>= 0.18 x [tidal difference (m) ]<br>/ [Hg elution rate from sample sediment] / [safety ratio] |
|  | River or lake sediment | Total mercury |  | 25 mg/kg (dw) |

Source: 1 Inter-Ministerial Coordination Council on the Minamata Convention on Mercury, Japan (2017).

*Table 9 Fish and other food items (mercury standards and guideline values)*

| Issued | Target | Parameter | Type | Value |
|---|---|---|---|---|
| USEPA[1] | Fish | methylmercury | Human health criteria | 0.3 mg/kg |
| USFDA[2] | Fish, shellfish, crustaceans, other aquatic animals (fresh, frozen or processed) | methylmercury in edible portion | Action level | 1 mg/kg |
|  | Wheat (pink kernels only) | pink kernels (an average of 10 or more pink kernels/500 g) |  | 1 mg/kg |
| EU[3] | Fishery products and muscle meat of fish excluding species listed below<br>*Except for the followings:<br>- brown meat of crab<br>- head and thorax meat of lobster and similar large crustacean | Total mercury | Maximum level in food stuff | 0.1 mg/kg (ww) |
|  | Muscle meat of fish (species defined) | Total mercury |  | 1.0 mg/kg (ww) |
| MOHLWJ[4] | Fish and shellfish<br>*Except for the followings:<br>- Tuna (tuna, swordfish, bonito)<br>- River water fish<br>- Deep sea fish (sting fish, alfonsin, sablefish, red queen crab, ivory shell, sharks) | Total mercury | Provisional standard | 0.4 mg/kg |
|  |  | Methylmercury (reference value) |  | 0.3 mg/kg |

Source: 1 USEPA (2001a). 2 United States of America, Food and Drug Administration FDA (2000). 3 EU (2006). 4 MOHW (1973).

*Table 10 Waste (mercury standards and guideline values)*

| Issued | Target | Type | Value | |
|---|---|---|---|---|
| USEPA | Sewage sludge[1] | Cumulative loading for sludge applied on agricultural, forest and publicly accessible lands | 17 mg/kg (dw) | |
| | | | 17 kg/hectare | |
| | | Annual loading rate for sludge sold or distributed for application to a lawn or home garden | 17 mg/kg (dw) | |
| | | | 85 kg/hectare | |
| | | Sludge sold or distributed for other types of land disposal | 57 mg/kg (dw) | |
| | Hazardous waste[2] | Hazardous waste regulation | 0.2 mg/L | Leaching test |
| MOEJ[3] | Slag, soot and dust, sludge | Specially controlled industrial waste regulation | 0.005 mg/L | If the waste contains 1000 mg/kg or more of mercury, mercury in it must be recovered. |
| | Waste acid, waste alkali | | 0.05 mg/L | If the waste contains 1000 mg/L or more of mercury, mercury in it must be recovered. |
| | Burn residue, slag, soot and dust, sludge | Regulation of mercury containing dust, etc. | 15 mg/kg | If the waste contains 1000 mg/kg or more of mercury, mercury in it must be recovered. |
| | Waste acid, waste alkali | | 15 mg/L | If the waste contains 1000mg/L or more of mercury, mercury in it must be recovered. |

Source: 1 USEPA (2018). 2 USEPA (2022b). 3 Japan, Inter-Ministerial Coordination Council on the Minamata Convention on Mercury (2017).

*Table 11 Air emissions (mercury standards and guideline values)*

| Issued | Facilities or equipment | | | Standard | |
|---|---|---|---|---|---|
| | | | | New established | Existing facility |
| USEPA | Coal- and oil-fired electric utility steam generating units[1] | Coal-fired unit | Not low rank virgin coal | $3.0e^{-3}$ lb/GWh | $1.2e^{+0}$ lb/TBtu or $1.3e^{-2}$ lb/GWh (Testing for 30 days)<br>$1.0e^{+0}$ lb/Tbtu or $1.1e^{-2}$ lb/GWh (Testing for 90 days) |
| | | | Low rank virgin coal | $4.0e^{-2}$ lb/GWh | $4.0e^{+0}$ lb/Tbtu or $4.0e^{-2}$ lb/GWh (Testing for 30 days) |

| Issued | Facilities or equipment | | | Standard | |
|---|---|---|---|---|---|
| | | | | New established | Existing facility |
| | | IGCC unit | | 3.0e$^{-3}$ lb/GWh | 2.5e$^{+0}$ lb/Tbtu or 3.0e$^{-2}$ lb/GWh (Testing for 30 days) |
| | | Liquid oil-fired unit | Continental (excluding limited-use liquid oil-fired subcategory units) | 1.0e$^{-4}$ lb/GWh | 2.0e$^{-1}$ lb/Tbtu or 2.0e$^{-3}$ lb/GWh |
| | | | Non-continental (excluding limited-use liquid oil-fired subcategory units) | 4.0e$^{-4}$ lb/GWh | 4.0e$^{-2}$ lb/Tbtu or 4.0e$^{-4}$ lb/GWh |
| | | Solid oil-derived fuel-fired unit | | 2.0e$^{-3}$ lb/GWh | 2.0e$^{-1}$ lb/Tbtu or 2.0e$^{-3}$ lb/GWh (Testing for 30 days) |
| | | Eastern Bituminous Coal Refuse-fired unit[2] | | - | 1.2e$^{+0}$ lb/Tbtu or 1.3e$^{-2}$ lb/GWh (Testing for 30 days)<br>1.0e$^{+0}$ lb/Tbtu or 1.1e$^{-2}$ lb/GWh (Testing for 90 days) |
| | Portland cement manufacturing industry[3] | | | 21 lb/million metric tons clinker | 55 lb/million metric tons clinker |
| | Large municipal waste combustors[4] | Combust greater than 250 tons per day of municipal solid waste | | 50 μg/m$^3$ (dscm@ 7 % $O_2$) | 50 μg/m$^3$ (dscm@ 7 % $O_2$) |
| | Small municipal waste combustors[5] | Combust from 35 to 250 tons per day of municipal solid waste | | 0.080 mg/m$^3$ (dscm @ 7 % $O_2$) | |
| | Commercial and industrial solid waste incineration units[6] | | | - | 0.016 mg/m$^3$ (dscm@ 7 % $O_2$) |
| | Sewage sludge incineration units[7] | Multiple hearth sewage sludge incineration | | 0.15 mg/m$^3$ (dscm @ 7 % $O_2$) | 0.28 mg/m$^3$ (dscm@ 7 % $O_2$) |
| | | Fluidized bed sewage sludge incineration | | 0.0010 mg/m$^3$ (dscm@ 7 % $O_2$) | 0.037 mg/m$^3$ (dscm@ 7 % $O_2$) |
| | Hospital/ medical/ infectious waste incinerators[8] | Large (>500 lb/hr of waste) | | - | 0.018 mg/m$^3$ (dscm@ 7 % $O_2$) |
| | | Medium (>200 to ≤500 lb/hr of waste) | | - | 0.025 mg/m$^3$ (dscm@ 7 % $O_2$) |

| Issued | Facilities or equipment | | | Standard | |
|---|---|---|---|---|---|
| | | | | New established | Existing facility |
| | | Small (≤200 lb/hr of waste) | | - | 0.014 mg/m$^3$ (dscm@ 7 % $O_2$) |
| | | Small rural (small facility >50 miles from boundary of nearest SMSA, burning <2,000 lb/week of waste) | | - | 0.0051 mg/m$^3$ (dscm@ 7 % $O_2$) |
| | Gold ore processing and production facilities | Ore pre-treatment processes | | 84 lb/million tons of ore | 127 lb/million tons of ore |
| | | Carbon processes with mercury retorts | | 0.8 lb/ton of concentrate | 2.2 lb/ton of concentrate |
| | | Carbon processes without mercury retorts | | 0.14 lb/ton of concentrate | 0.17 lb/ton of concentrate |
| | | Non-carbon concentrate processes | | 0.1 lb/ton of concentrate | 0.2 lb/ton of concentrate |
| MOEJ[9] | Coal fired power plant<br>Industrial coal combustion boiler | Coal-fired boiler<br>Large coal mixed combustion boiler | | 8 µg/Nm$^3$ | 10 µg/Nm$^3$ |
| | | Small coal mixed combustion boiler | | 10 µg/Nm$^3$ | 15 µg/Nm$^3$ |
| | Process of refining and roasting used for manufacturing nonferrous metals (copper, lead, zinc and industrial gold) | Primary facility | Copper or industrial gold | 15 µg/Nm$^3$ | 30 µg/Nm$^3$ |
| | | | Lead or zinc | 30 µg/Nm$^3$ | 50 µg/Nm$^3$ |
| | | Secondary facility | Copper, lead or zinc | 100 µg/Nm$^3$ | 400 µg/Nm$^3$ |
| | | | Industrial gold | 30 µg/Nm$^3$ | 50 µg/Nm$^3$ |
| | Equipment for incineration of waste | Waste incinerator（Municipal waste / industrial waste / sewage sludge incinerator） | | 30 µg/Nm$^3$ | 50 µg/Nm$^3$ |
| | | Incinerators such as mercury-containing sludge etc. | | 50 µg/Nm$^3$ | 100 µg/Nm$^3$ |
| | Equipment for manufacturing cement clinker | Firing furnace provided for manufacturing cement | | 50 µg/Nm$^3$ | 80[3] µg/Nm$^3$ |

Source: 1 USEPA (2016a). 1 lb = 454 g, 1 lb/GWh = 454 g/GWh, 1 lb/Tbtu = 1.55 g/GWh. 2 New category established by USEPA (2020). 3 USEPA (2012). 4 USEPA (2006) 5 USEPA (2000). 6 USEPA (2016b). 7 USEPA (2011). 8 USEPA (2013). 9 Japan, Inter-Ministerial Coordination Council on the Minamata Convention on Mercury (2017). Existing facilities means the facilities built before April 2018.

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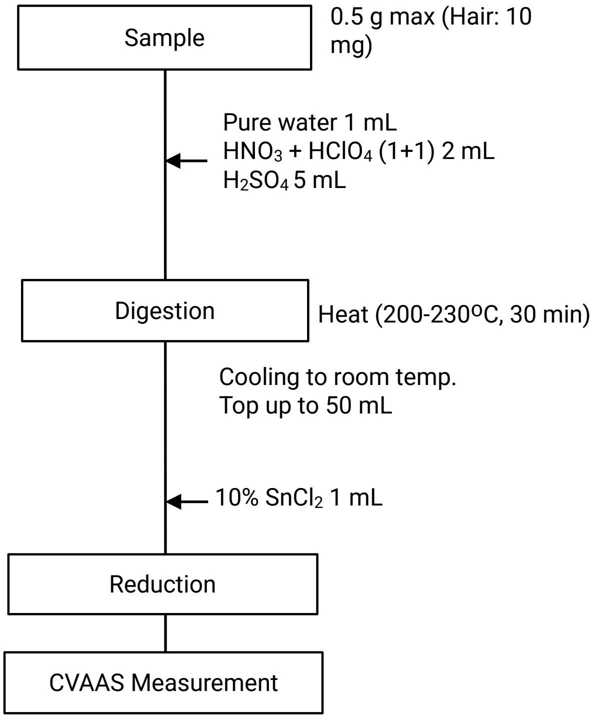
[3] For raw material limestone those having a mercury content of 0.05 mg or more in 1 kg, standard is 140 µg /Nm$^3$

*Table 12 Hair and blood (reference value corresponding to mercury tolerable intake)*

| Issued | Target | Parameter | Type | Value |
|---|---|---|---|---|
| WHO[1] | Prenatal exposure to methylmercury on child neurodevelopment | Methyl-mercury | Provisional tolerable weekly intake (PTWI) | 1.6 µg/kg (bw)-week<br>- Based on BMDL/NOEL derived from 14 mg/kg of maternal hair, which is equivalent to a maternal blood methylmercury concentration of 0.056 mg/L.<br>- Daily intake of methylmercury of 1.5 µg/kg (bw) is divided by a total uncertainty factor of 6.4 to give a value of 1.6 µg/kg (bw) in weekly basis.<br>- Hair mercury concentration divided by the uncertain factor of 6.4 is 2.2 mg/kg. |
|  | Adult | Methyl-mercury |  | Intakes of up to about two times higher than the PTWI of 1.6 µg/kg (bw)-week would not pose any risk of neurotoxicity in adults.<br>- Hair mercury concentration about two times higher than the level of the PTWI is 4.4 mg/kg. |
|  | Infant and children aged up to about 17 years | Methyl-mercury |  | No clear line drawn<br>- Clearly not more sensitive than the embryo or fetus but might be more sensitive than adults. |
| USEPA[2] | Offspring at 7 years of age | Methyl-mercury | Oral reference dose (RfD) for developmental neuropsychological impairment | *14.1* µg/kg (bw)-day<br>- Derived from integrated analysis of benchmark dose levels ranging between 0.046 mg/L and 0.079 mg/L of maternal cord blood corresponding to 11 mg/kg and 20 mg/kg of maternal hair.<br>- Uncertainty factor 10 applied to corresponding values of maternal daily intakes of 0.857-1.472 µg/kg (bw)-day.<br>- Hair mercury concentration divided by uncertain factor of 10 is between 1.1 mg/kg and 2.0 mg/kg. |

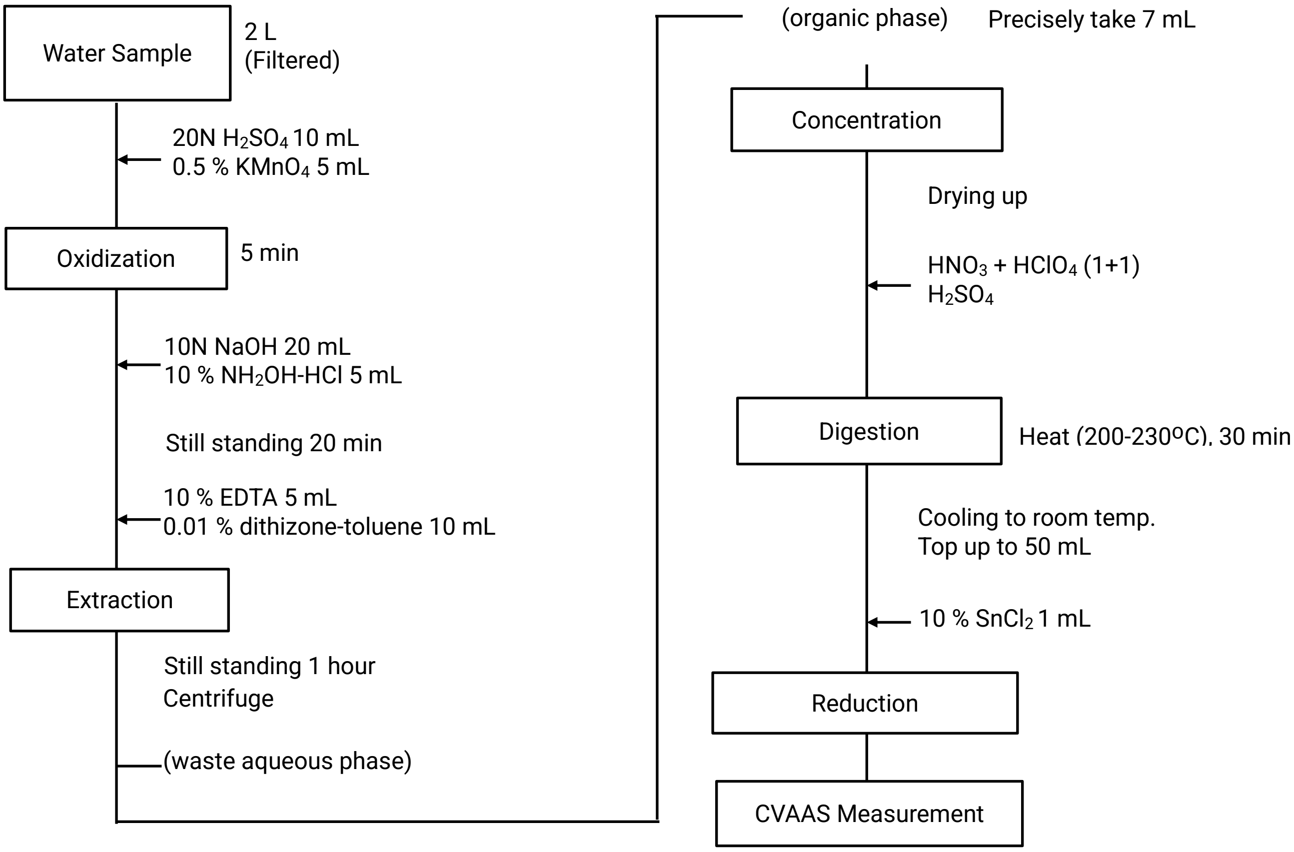
Source: 1 Joint FAO/WHO Expert Committee on Food Additives JECFA (2007). 2 USEPA (2001b).

# 4.3 Process flows



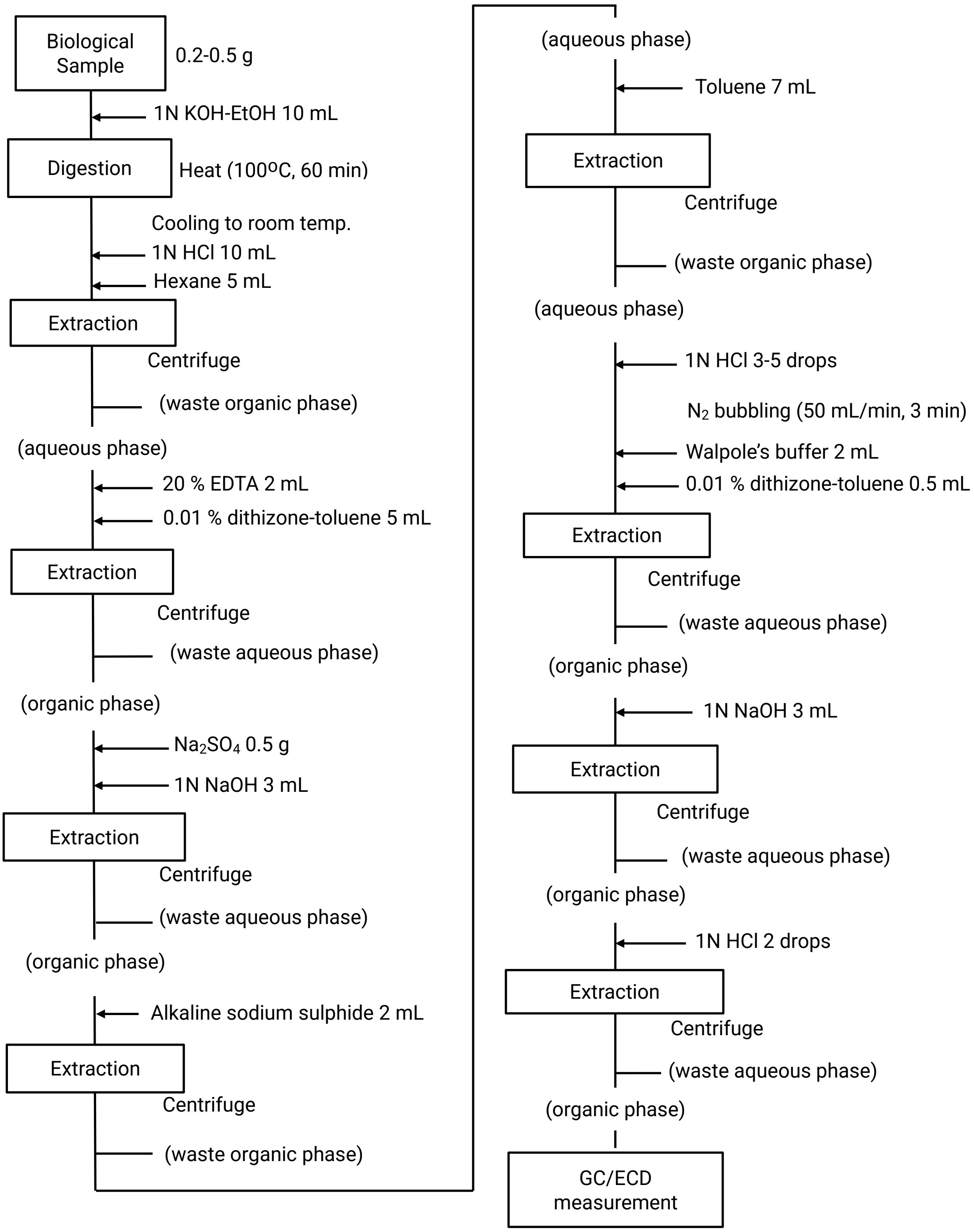
Japan, Ministry of the Environment (2004). Mercury analysis manual. March 2004.

*Figure 1 Flowchart of total mercury analysis by acid digestion – aeration CVAAS*



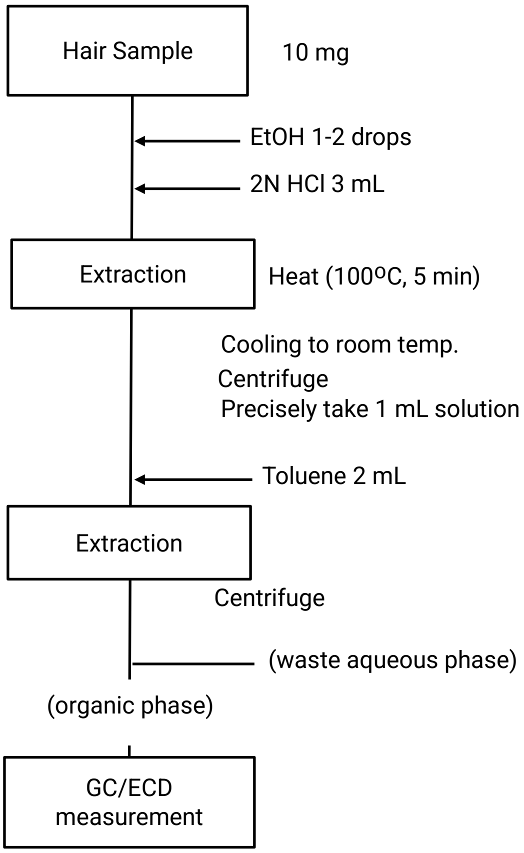
Japan, Ministry of the Environment (2004). Mercury analysis manual. March 2004.

*Figure 2 Flowchart of total mercury analysis in water by dithizone extraction aeration CVAAS*



Japan, Ministry of the Environment (2004). Mercury analysis manual. March 2004.

*Figure 3* Flowchart *of methylmercury analysis in biological sample by dithizone extraction GC/ECD*



Japan, Ministry of the Environment (2004). Mercury analysis manual. March 2004.

*Figure 4 Flowchart of methylmercury analysis in hair sample by HCl extraction GC/ECD*

# 4.4 List of certified reference materials

*Table 13 Certified reference materials of mercury*

| Category | Material | T-Hg | MeHg | Manufacturer |
|---|---|---|---|---|
| Hair | Human hair powder | X | X | International Atomic Energy Agency |
| Food | Lichen powder, Cabbage powder | X | | |
| Biota | Freeze-dried tuna meat, Freeze-dried scallop, Cotton cellulose powder, Freeze-dried clam | X | X | |
| Sediment | Lake sediment, Coastal sediment, Marine sediment | X | | |
| Urine | Frozen human urine | X | | National Institute of Standards and Technology |
| Biota | Oyster tissue, Lake Superior fish tissue, Lake Michigan fish tissue, Bovine liver | X | X | |
| Sediment | Estuary sediment, New York/New Jersey Waterway Sediment, Inorganics in marine sediment, Sediment for solid sampling | X | | |
| Soil | Soil containing lead from paint, New Jersey soil, San Joaquin soil, Montana soil | X | | |
| Plant | Apple leaves, Peach leaves, Spinach Leaves, Tomato leaves, Pine needles | X | | |
| Food | Typical diet, Wheat flour, Rice flour, Green tea leaves | X | | |
| Waste | Hard rock mine waste, Domestic sludge, Industrial sludge | X | | |
| Biota | Dogfish liver, Fish protein, River prawn, Cuttlefish, Lobster Hepatopancrea | X | X | National Research Council Canada |
| Sediment | Marine sediment | X | | |
| Hair | Human hair powder | X | X | National Institute for Environmental Studies |
| Biota | Freeze-dried fish meat powder | X | | |
| Soil | Air-dried sieved soil | X | | |
| Hair | Human hair powder | X | X | National Institute for Minamata Disease |
| Urine | Human urine (high concentration, low concentration) | X | | |
| Soil | Forest soil, Hg added forest soil | X | | Japan Society for Analytical Chemistry |
| Soil | Heavy meal added forest soil | X | | |
| Sediment | Marine sediment, Lake sediment | X | | National Metrology Institute of Japan |
| Biota | Freeze-dried cod meat, Freeze-dried swordfish tissue | X | X | |

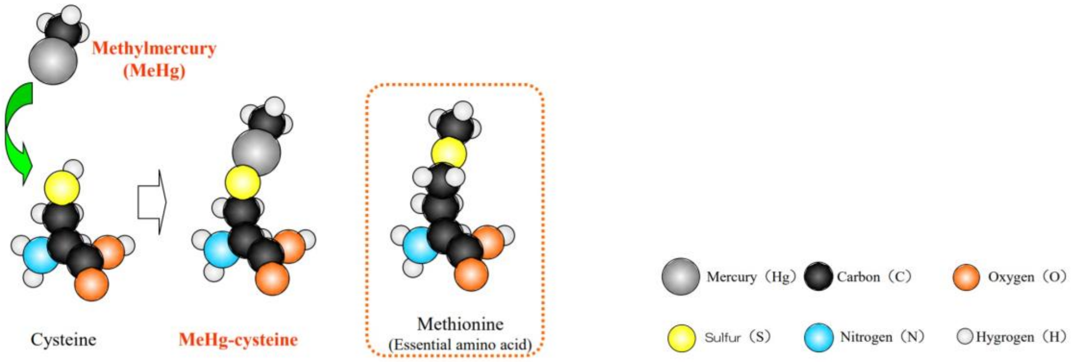
## 4.5 Physical and chemical properties, usage, and environmental behaviours of mercury

### Physical and chemical properties of mercury

Mercury is a chemical element that exists in various forms with unique physical properties. With an atomic number of 80, which is next to gold, mercury is the only metal element that exists in liquid form at normal temperatures. In addition, mercury has a low boiling point among metallic elements, and it is volatile with high a vapour pressure. The abundance of mercury in Earth's crust is similar to that of silver, but mercury has a much lower market price than precious metals.

*Table 14 Physical properties of elemental mercury*

Atomic number: 80
Atomic weight: 200.59
Melting point: -38.8 °C
Boiling point: 356 °C
Specific gravity: 13.6 at 0 °C
Thermal conductivity: 8.3 W/m°C
Saturated vapor concentration: 13.2 mg/$m^3$ at 20 °C
Abundance in Earth's crust: 0.05 – 0.08 ppm
Emission spectrum at ultra-violet band: 254 nm (UV-C)
Forming amalgam with many metallic elements



Source: Japan, National Institute for Minamata Disease (2013). Mercury and health V4.1.

*Figure 5 Molecular similarity of methylmercury-cysteine complex and methionine*

Methylmercury is a mercury compound of great concern due to its high toxicity. Methylmercury binds cysteine, a kind of amino acid, to form a complex with a molecular structure similar to methionine, an essential amino acid (Figure 5). Due to this similarity, the complex is actively absorbed via an amino acid transporter. Then, it is incorporated into body tissues made of protein including the brain and fetus.

Most mercury and mercury compounds have certain toxicities, but their biological behaviours and toxicity levels differ. Main exposure pathways, symptom and treatment for three (3) types of mercury and mercury compounds are shown in Table 15. The absorption rates of inhaled elemental mercury and ingested methylmercury are very high, while the absorption rate of inorganic mercury is rather low. Ingested elemental mercury is usually directly excreted without absorption. Absorbed mercury is gradually oxidized and excreted in urine as inorganic mercury. Elemental mercury passes through the blood-brain barrier and causes mercury poisoning of the central nervous system. Accidental high-level exposure to mercury vapour in the workplace can be fatal, but acute symptoms are usually reversible. The symptoms of chronic low-level exposure to elemental mercury were known as mad hatter's disease. Methylmercury is transported actively to form body tissues made of protein. The adverse effects depend on the body parts into which methylmercury is incorporated. Ingested inorganic mercury causes inflammation of the digestive tract and kidney damages if the amount is very high. Acute mercury exposure is usually treated by stimulating the excretion. For chronic exposure, stopping exposure is the most important measure.

*Table 15 Exposure pathway, symptom and treatment*

| | Elemental Mercury | Inorganic Mercury | Methylmercury |
|---|---|---|---|
| Exposure pathway (absorption rate) | - Inhalation (75-85 %)<br>- Ingestion (0.01 % or less). | - Ingestion (5-10 % or less)<br>- Dermal (not expected to be high). | - Ingestion (90 % or more) |
| Behaviour and fate | - Unoxidized form passes through blood-brain barrier (by diffusion)<br>- Gradually oxidized to divalent inorganic mercury | - Excreted in urine | - Passes through blood-brain and placenta barrier (by amino acid transportation)<br>- Gradually oxidized to divalent inorganic mercury |

| | Elemental Mercury | Inorganic Mercury | Methylmercury |
|---|---|---|---|
| Symptom | - Respiratory distress<br>- Central nervous system effects (tremor, personality change, tooth pain, excessive salivation)<br>- Referred to as 'mad hatter's disease' | - Corrosion in digestive tract (vomiting, chest pain, abdominal pain, and bloody diarrhoea)<br>- Kidney damage<br>- Renal insufficiency | - Central nervous system effects (sensory nerve dysfunction, ataxia, and constriction of visual field)<br>- Fetal exposure (non-specific cerebral palsy-like features) |
| Treatment | - Stimulation of mercury excretion | - Gastric lavage, excretion with chelating agent | - No effective treatment |

Source: Japan Public Health Association (2001). Preventive Measures against Environmental Mercury Pollution and Its Health Effects.

## Mercury products and uses

Mercury is one of a few elements known since ancient times. It has been used for various purposes for many thousands of years as shown in Figure 6. Red pigments and the preservation of corpses are among the oldest applications. The demand of mercury has increased as new uses have been invented over time. The supply side, that is mercury mining, has also been well developed to support the demand for mercury. Today, some mercury-added products and processes have been replaced by non-mercury alternatives, but many are still widely used globally. The Minamata Convention controls the products and processes stipulated in the Annexes, but even after phase out, mercury waste will continue to be generated for a long time. Thus, proper management of mercury waste is very important.

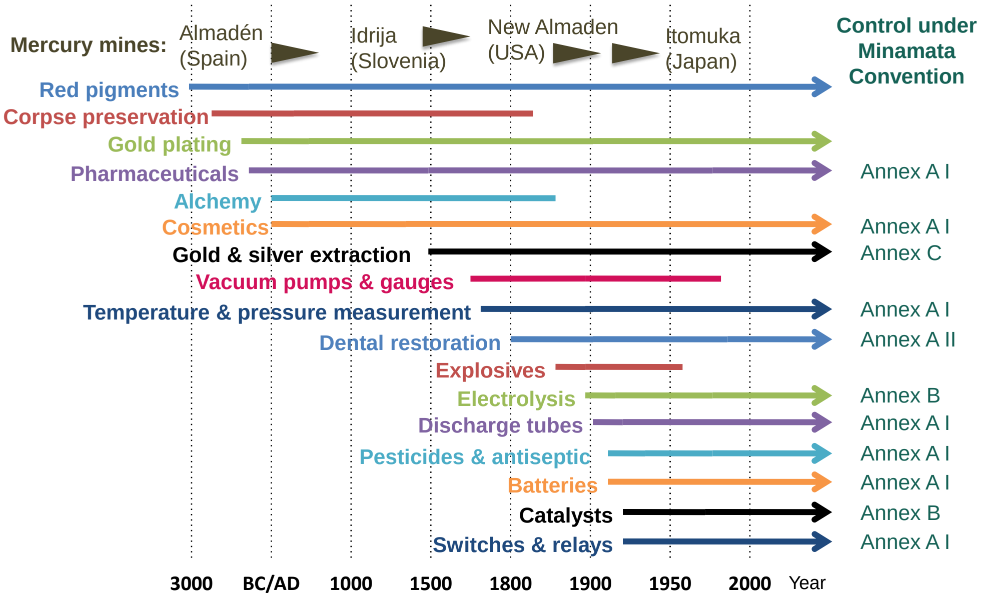
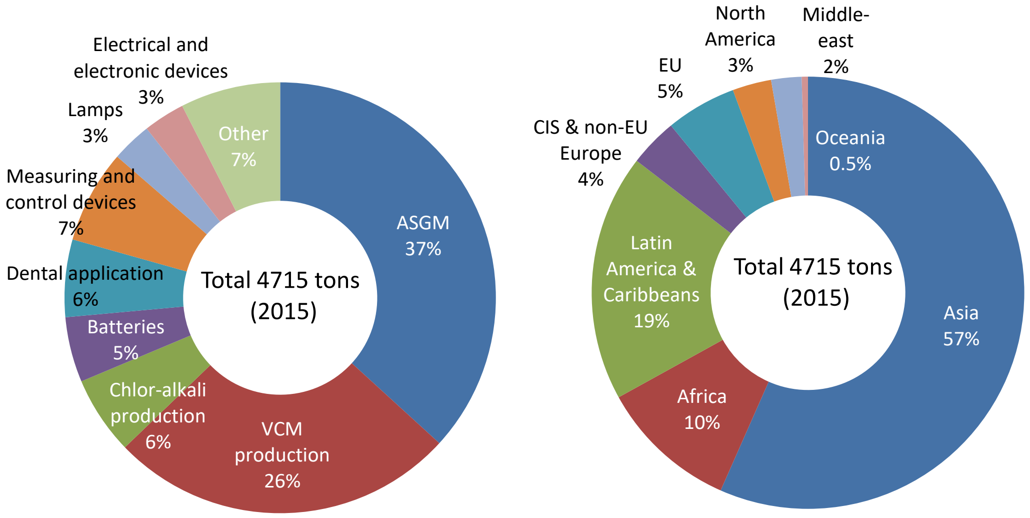


*Figure 6 Historical mercury supply and use*

As shown in Figure 7, global mercury use is estimated to be approximately 4700 tons per year as of 2015. Artisanal and small-scale gold mining is the largest mercury consumer, and Asia, Africa, Latin America and the Caribbean are the regions consuming a large amount of mercury.



Source: United Nations Environment Programme (2017). Global mercury supply, trade and demand.

*Figure 7 Global mercury uses by sector and by region*

## Use of elemental mercury

Elemental mercury is used for measuring purposes. As a high-density liquid, it is suitable for measuring pressure. Devices such as manometers, barometers, and sphygmomanometers, enable precise pressure measurement without using electricity. For official purposes, “mmHg” or “inHg” can still be used as non-SI units of measurement. Mercury is also useful for measuring temperature because it exists in liquid form in a wide temperature range (-38.8 °C to 356 °C). As a metallic element, mercury has a high thermal conductivity, which provides a quick response. Some mercury-added measuring devices are subject to phase out under the Minamata Convention.

A discharge tube is an electronic device that contains gas or vapour at low pressure, and through which conduction takes place when a high voltage is applied. The mercury arc rectifier was an important device for converting high voltage alternating current (AC) to direct current (DC). As modern electricity supply networks were developed with AC, rectification was required if the industry required DC. Today, this function is mostly performed by power semiconductors. Several gaseous elements, including mercury vapour, emit various wavelengths of light. Mercury discharges ultra-violet ray (UV-C) which is invisible to humans. As UV-C damages DNA, mercury vapour lamps are used for microbial disinfection. Fluorescent lamps convert UV-C to visible light for lighting applications. The light emitted from discharge tubes are also used for various lighting applications, such as indoor and outdoor lighting, signage, and the headlamps of vehicles.

As mercury is electrically conductive, it is used for various electric controls. The mercury switch has several advantages for closing and opening electrical circuits. As the contact surface is concealed, no oxidation occurs, and the surface remains clean with a low resistance due to the wetting nature of mercury. Application includes tilt switches to activate lights on the boot lids of vehicles, rollover warning device for vending machines, anti-lock braking systems that detect acceleration force, high-speed switch as mercury relay does not cause chattering, and mercury slip rings that transmit signals or power to devices over 360° of rotation.

Mercury is added to batteries for safety purposes to prevent hydrogen gas generation. Abnormal reactions at the zinc anode causes cell rupture or leakage, but mercury inhibits such abnormal reactions. Although most dry cells have stopped using mercury, a few types of button cells still use mercury for this purpose. Lithium coin cells do not use water as the electrolyte, so no mercury is added.

Elemental mercury is also used for many other purposes. Some are being phased out as non-mercury alternatives are becoming increasingly available. It is important to be aware that not all uses of mercury are subject to the Minamata Convention, so legitimate uses of mercury will remain. The applications of elemental mercury are summarized in Table 16

*Table 16 Applications of elemental mercury*

| Type | Theory / Principle | Application | Remarks |
|---|---|---|---|
| Measuring devices | - High density liquid | - Manometer (pressure in system, facility, etc.)<br>- Barometer (atmospheric pressure)<br>- Sphygmomanometer (blood pressure) | - No electric supply required.<br>- No equivalent alternative for high temperature devices.<br>- Extensively used for measuring blood pressure. |

| Type | Theory / Principle | Application | Remarks |
|---|---|---|---|
| Ditto | - Liquid in wide temperature range<br>- High thermal conductivity | - Thermometer (temperature)<br>- Hygrometer (wet bulb, relative humidity) | - No electric supply required.<br>- Quick response.<br>- No equivalent alternative for high temperature device. |
| Discharge tubes | - Electric valve effect | - Mercury arc rectifier (rectifying high voltage AC to DC) | - Large power supply capacity for industries requiring DC.<br>- Largely replaced by power semiconductors. |
| Ditto | - Emitting UV-C (254nm) | - Neon lamp (signage, display)<br>- Fluorescent lamp (lighting)<br>- High-pressure discharge lamp (projection, lighting, sun tanning, headlamp of vehicles)<br>- Low pressure mercury vapour lamp (disinfection) | - No filament in bulb, long life.<br>- UV-C emitting efficiency is higher than LED. |
| Switches and relays | - Electrically conductive liquid<br>- Wetting effect on contact surface | - Tilt switch/alarm (activating lights for boot lids of vehicles)<br>- Acceleration censor (anti-lock braking systems)<br>- Mercury-wetted relay (power/signal transmission for 360° rotating devices) | - Low resistance and no chattering at contact surface.<br>- Allows high frequency switching. |
| Batteries | - Hydrogen overpotential | - Button cell (preventing hydrogen gas generation at zinc anode) | - Lithium coin cell does not use water, thus no mercury is added. |
| Vacuum pumps | - High density liquid<br>- Air induction | - Mercury column pump (1Pa)<br>- Mercury rotary pump ($10^{-2}$Pa)<br>- Mercury diffusion pump ($10^{-3}$Pa) | - Replaced with oil-based fluid. |
| Balancers | - High density liquid | - Wheel balancer<br>- Trim and heel controller (submarine) | - Non-mercury (solid) balancers are available. |
| Laboratory instruments | - High surface tension | - Porosimeter | - Used to analyse porosity of material surfaces. |
| Fluid bearings | - High density liquid | - Lighthouse rotation unit | - Floating Fresnel lens. |
| Electric conductors | - Electrically conductive liquid | - Slip ring (360° rotation) | - Brushless contact. |
| Mirrors | - Liquid with high reflectance | - Liquid zenith telescope | - Rotating mirror to form paraboloid mirror. |
| Propellants | - Easy ionization | - Ion thruster (satellites) | - Replaced by xenon. |

## Use of amalgam

Mercury can form various alloys with other metals, which are called amalgam. Amalgam has been an important material for many industries as final products or in production processes. Dental amalgam is a mixture of silver and tin powder, which is gradually hardened to fill dental cavities. Tin amalgam was used for the reflective surfaces of mirrors.

Gold and silver extraction and refining have been practised for many thousands of years. The oldest method called cupellation used lead and was invented in BC era. There was a risk for lead poisoning with this method. The amalgamation method was then invented in the 16th century when silver mining in Latin America was at its peak. Due to the melting and boiling points of mercury being lower than those of lead, the consumption of heat sources, i.e., firewood, was reduced, which preserved forests in the region. The amalgamation method for ASGM accounts for the largest usage of mercury today and disproportionally affects marginalised and less privileged groups. The cyanide method was invented in the late 19th century during the Gold Rush era. This method is currently predominantly used for large-scale gold mining operations, but its application to ASGM is being explored.

NaCl, which is the chemical form of edible salt, can generate chlorine gas and caustic soda by electrolysis. Caustic soda is used for manufacturing products such as soap and glass, and chlorine gas is used for producing disinfection and bleaching agents as well as PVC. Mercury is used as the electrode for the mercury-cell process, which was invented in the early 20th century and still is used in some countries. Chlorine ions are oxidized at the anode and become chlorine gas. On the cathode side, where mercury is used, sodium ions are reduced to metallic sodium, which forms an amalgam with mercury. The sodium amalgam is then sent to an amalgam decomposer, where caustic soda is formed. The key to this electrolysis process is blocking sodium backflow to the anode side. The diaphragm process physically blocks this backflow with the fibrinous structure of asbestos. This system is still used but the risk of asbestos is a concern. The membrane process has a similar configuration to the diaphragm process, but an ion exchange membrane allows the selective permeation of sodium ions to the cathode side, which is more energy efficient and avoid toxic substances.

Special applications of amalgam include low-temperature thermometers with thallium amalgam, which is melting temperature of approximately minus 60 °C. However, mercury is problematic in the oil and gas sector. Mercury erodes aluminium equipment, such as heat exchangers, and inactivates palladium-based catalysts. The applications of amalgam are summarized in Table 17.

*Table 17 Applications of amalgam*

| Type | Theory / Principle | Application | Remarks |
|---|---|---|---|
| Dental filling | - Gradually hardening after mixing | - Dental cavity restoration (filling silver tin amalgam into dental cavities) | - No electric supply required.<br>- Mercury waste is released into drainage.<br>- Mercury is gradually vapourised in the mouth. |
| Gold/ silver industry | - Absorption of metallic elements<br>- Low boiling point | - Gold/silver extraction (predominantly used for ASGM)<br>- Gold plating (gold amalgam is smeared on metallic surface and then heated) | - Workers and some community members are exposed to mercury vapour.<br>- Cyanide method is an alternative for extraction but requires higher management skill. |
| Mirror surfaces | - Gradually hardening after mixing | - Mirror (tin amalgam forms the reflective surfaces) | - Replaced by silver mirror reaction. |
| Electrolysis | - Absorption of metallic elements | - Chlor-alkali production (separating sodium from brine after electrolysis) | - Ion exchange membrane process is an alternative with a higher energy efficiency. |
| Measuring devices | - Low temperature alloy | - Low temperature thermometer | - Melting temperature of thallium amalgam is -60°C. |
| Oil and gas (problematic) | - Creating unwanted amalgam | - Aluminium equipment (eroding surface of equipment)<br>- Palladium catalyst (inactivating the catalytic function) | - Mercury removal process should be installed in the system. |

**<u>Use of mercury compounds</u>**

Mercury sulphide is naturally found as cinnabar, which exists as blood red crystals or dark red stones. Red is one of the oldest colours that humans have intentionally used since the pre-historic era. Three major red pigments have been used. Iron oxide provides brownish red, and is easily available from red clay soil. By contrast, mercury sulphide needs laborious refinement from ore, so it was an expensive pigment. It can also be synthesized from mercury and sulphur. Due to its preciousness, mercury sulphide was used for more important occasions, such as ceremonial and religious purposes. Lead oxide is also a synthesized pigment with a bright orange colour.

Cosmetics also use colour, which are predominantly consumed by women. Red, white, and black are the three base colours for cosmetics. Red pigments, such as cinnabar, were used for bodypainting in some indigenous societies. More broadly, white face powder has been used for makeup. Calomel, mercury (I) chloride, is a white powder used for such purposes. Other chemicals, including lead white and talc, have also been used. Lead poisoning by face powder was problematic in the past few centuries. Currently, concerns have been raised about talc, which contains asbestos as an impurity. Mercury use for skin-whitening cream is another concern, as it is still widely used globally. The preference to lighter coloured skin is still prevalent in many countries where the skin care industry keeps feeding illegal products into market.

The 'biocidal action' of mercury is used for fungicides and preservatives. Organic mercury compounds such as phenylmercury have been used for seed dressing, as fungicides for crops such as rice and wheat. Among inorganic mercury compounds, mercury chloride has been used for wood preservation, and red mercury oxide has been used for anti-fouling ship paint. In some products that are directly applied to humans, mercury compounds are still used as preserving agents. For example, thiomersal preserves vaccines at normal temperatures, which is important when providing vaccines to remote areas where no cold chain is available.

Mercury has been used in pharmaceuticals since ancient times. Traditional Chinese and Ayurveda medicines still include mercury products. One of the most significant historical uses of mercury for pharmaceutical purposes is the treatment of syphilis patients. Syphilis emerged in the late 15th century and rapidly spread over the globe. Many types of mercury compounds were used for medical treatment from the 16th century, until being replaced by penicillin in the 1940s. Mercurochrome is a water solution of the organic mercury compound merbromin, which was invented in the early 20th century and has been widely used for treating minor wounds. Its less painful nature and cheap price allowed various applications in both clinical and household settings. Mercury inhibits the growth of microorganisms. This characteristic has been used for many preservation and antiseptic purposes.

A catalyst is a substance that facilitate or accelerates a chemical reaction, but its form remains unchanged. The elements in the zinc group, which includes mercury, have been used as catalysts for organic synthesis, particularly for the production of vinyl polymers by accelerating addition reactions from acetylene. The catalysts form intermediate compounds to promote addition reactions. Minamata disease was caused by the mercury catalyst, mainly mercury (II) sulphate, used for acetaldehyde production, which was methylated in the factory and then released into the environment. To avoid the use of mercury, ethylene can be used for the feedstock instead of acetylene. Another type of catalyst is the initiator for polymerising polyurethane elastomer, called latent catalyst, which triggers the process in moulded products or coating. There are many types of mercury and non-mercury catalyst used as the latent catalyst, among which phenylmercury acetate is commonly used for this purpose. Although mercury acts as a catalyst for this process, it remains in the final product.

Batteries, especially chemical batteries utilize the oxidation and reduction of chemical compounds to store electricity. The mercury cell is a type of battery that has mercury oxide cathode. Once electricity is consumed, mercury oxide is reduced to metallic mercury, which flows out of the cathode. This product is subject to phase out under the Convention. However, mercury use for research, calibration, and reference is exempted from the Convention, so standard cells such as the Weston cell are not subject to phase out.

Various mercury compounds are used for many other purposes. One of historical uses is mercury (II) nitrate for hat making. A process called 'carroting' was extensively used for the preparation of felt. Mercury (II) fulminate was also an important mercury compound used extensively during wars as a material for the detonation caps of explosives. A new use has been examined for mercury (II) sulphide for the final disposal of mercury waste because stabilisation is required in some countries to dispose of mercury. The applications of mercury compounds are summarized in Table 18

*Table 18 Applications of mercury compounds*

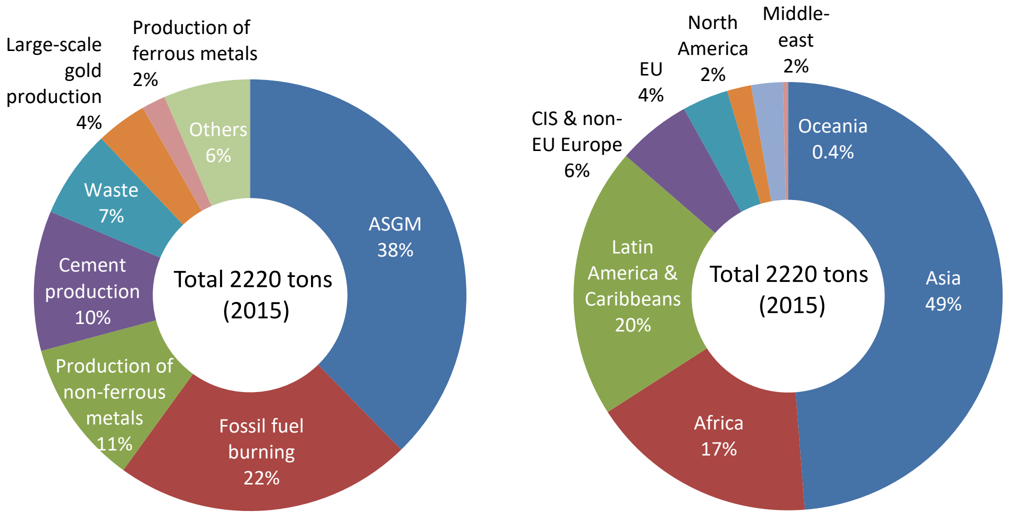
| Type | Theory / Principle | Application | Remarks |
|---|---|---|---|
| Mercury sulphide/ cinnabar | - Low solubility and stable chemical form.<br>- Reddish colour | - Red pigment (vermillion refined from cinnabar or synthesised from mercury and sulphur).<br>- Bodypainting (ancient indigenous custom)<br>- Waste mercury (stabilisation for final disposal) | - Iron oxide (brownish red ochre) and lead oxide (bright orange red) have also been used. |
| Mercury (I) chloride / calomel | - Bactericidal & fungicidal actions<br>- White colour<br>- Stable electrode potential | - Pharmaceuticals (syphilis)<br>- White face powder<br>- Saturated calomel electrode | - Lead white (lead poisoning), talc (contaminated with asbestos).<br>- Silver chloride reference electrode is an alternative. |
| Mercury (II) oxide | - Forming liquid mercury once reduced<br>- Biocidal action | - Battery (cathode for mercury cell)<br>- Antifouling paint for ship's bottom | - Mercury cell has been replaced with non-mercury alternatives.<br>- Replaced with copper-based ship paint. |

| Type | Theory / Principle | Application | Remarks |
|---|---|---|---|
| Mercury (II) sulphate | - Forming intermediate with acetylene<br>- Forming liquid mercury once reduced | - Catalyst (acetaldehyde production)<br>- Weston standard cell (producing highly stable voltage for calibration) | - Acetylene-based acetaldehyde production has been replaced with ethylene-based system. |
| Mercury (II) nitrate | - Fulling fur | - Carroting (preparation of felt) | - Extensively used for hat making in the 19th century. |
| Mercury (II) chloride | - Bactericidal & fungicidal actions<br>- Water solubility<br>- Reduce silver halide (photo)<br>- Forming intermediate with acetylene | - Fungicide (wood preservation, seed dressing)<br>- Preservative (pulp & paper)<br>- Standard solution (mercury analysis)<br>- Push-processing for photo, motion picture and X-ray films<br>- Catalyst (vinyl chloride monomer production) | - Volatile compound, which sublimates easily. |
| Ammoniated (II) mercury | - Bleaching effect<br>- Inhibition of bacterial growth | - Skin whitening cream (bleaching melamine)<br>- Antiseptic ointment | - Widely used in developing countries. |
| Phenylmercury | - Bactericidal & fungicidal actions<br>- Initiating polymerization reaction | - Fungicide (seed dressing against rice blight)<br>- Preservative (for latex paint, pulp & paper)<br>- Latent catalyst (polyurethane elastomer) | - Widely used in paddy fields. |
| Thiomersal | - Bactericidal action | - Preservative (vaccine and eye area cosmetics) | - Vaccine can be stored at normal temperature without refrigeration. |
| Merbromin | - Inhibition of bacterial growth<br>- Water solubility | - Mercurochrome (topical antiseptic for minor wound) | - Less absorbed from skin surface (due to hydrophilic nature). |
| Mercury (II) iodide | - Thermochromism | - Thermochromic paint | - Alter crystal structure at certain temperature. |
| Mercury (II) fulminate | - Explosiveness | - Detonation cap (blasting dynamite, bullet cartridge) | - Replaced by DDNP. |
| Mercury (II) thiocyanate | - Chemical reaction spewing out ash | - Pharaoh's snake (firework) | - Generating toxic smoke and residue |

## **Mercury emissions and releases and its risks**

As a chemical element, mercury has existed on Earth since its creation. Mercury is released from natural sources by processes, such as volcanic activity and permafrost melting. Once released, mercury poses risks to human health and the environment. In recent years, more mercury has been released through human activities, such as the combustion of fuels, mining activities, and the consumption of mercury-added products. Mercury is a trace element found in many minerals and fuels such as coal, natural gas, oil, non-ferrous ore. Mercury emitted to the atmosphere remains for a long time and will be transported long distances. Atmospheric mercury is gradually oxidized and deposited in the ocean or on land. Inorganic mercury in water bodies can be methylated by microbial activity, and bioaccumulated in biota at higher trophic levels. Eventually, fishing brings mercury back to human society through consumption. Excessive exposure to mercury, especially methylmercury, will pose risk to vulnerable population and pregnant women, in particular, as the methylmercury actively passes through placenta barrier by amino acid transporter to fetus.

Similar to mercury usage, the largest mercury emission source is ASGM, which disproportionally affects marginalised and less privileged groups, such as children and women of child-bearing age. Asia, Africa, Latin America and the Caribbean are the regions emitting large amounts of mercury as shown in Figure 8. The burning fossil of fuel and the production of cement and non-ferrous metals all removes mercury from the soil and emit it to the atmosphere. More importantly, such mercury by-product might increase with the economic development of developing countries.



Source: United Nations Environment Programme (2019). Global mercury assessment 2018.

*Figure 8 Global atmospheric mercury emissions by sector and by region*

# 4.6 Reference literatures and websites

Due to the Minamata Convention, a lot of literatures on mercury data are published from many countries. The Minamata Convention and the UNEP Global Mercury Partnership provide platforms to access relevant information.

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# 4.7 Glossary, acronyms, and abbreviations

| | |
|---|---|
| AAS | Atomic absorption spectrometry |
| AC | Alternate current |
| AIT | Asian Institute of Technology |
| ASGM | Artisanal and small-scale gold mining: gold mining conducted by individual miners or small enterprises with limited capital investment and production. |
| BAT | Best Available Techniques: Techniques that are the most effective to prevent and, where that is not practicable, to reduce emissions and releases. |
| BEP | Best Environmental Practices: Application of the most appropriate combination of environmental control measures and strategies. |
| BMDL | Benchmark dose limit |
| Btu | British thermal unit = 0.293 Wh |
| bw | Body weight |
| CAS | Chemical Abstracts Service |
| COP | Conference of the Parties |
| CRM | Certified reference material |
| CVAAS | Cold-vapour atomic absorption spectrometry |
| CVAFS | Cold-vapour atomic fluorescence spectrometry |
| DC | Direct current |
| DDNP | Diazodinitrophenol |
| dscm | Dry standard cubic metre: Amount of gas free of water vapour at a temperature of 20 °C and a pressure of 101325 Pa. |
| dw | Dry weight |
| ECD | Electron capture detector |
| EGU | Electric utility steam generating unit |
| EMC | Indonesia, Environmental Monitoring Centre |
| EMS | Environmental management system |
| ETDA | Ethylenediaminetetraacetic acid |
| EU | European Union |
| FY | Fiscal year |
| GC | Gas chromatography |
| GEF | Global Environment Facility |
| GEM | Gaseous elementary mercury |
| GOM | Gaseous oxidized mercury |
| GUM | Guide to the expression of uncertainty in measurement |
| IDEA | IDEA Consultants |
| IEC | International Electrotechnical Commission |
| IGCC | Integrated gasification combined cycle |
| ILO | International Labour Organization |
| lb | Pound = 454 g |
| ISO | International Organization for Standardization |
| JCGM | Joint Committee for Guide in Metrology |
| JECFA | Joint FAO/WHO Expert Committee on Food Additives |
| LED | Light-emitting diode |
| LOD | Limit of detection |
| LOQ | Limit of quantification |
| MOEJ | Japan, Ministry of the Environment |
| MOHLWJ | Japan, Ministry of the Health, Labour and Welfare |

| | |
|---|---|
| MOHWJ | Japan, Ministry of the Health and Welfare |
| MOLJ | Japan, Ministry of the Labour |
| MOYAI Initiative | A Japan’s commitment made at the Diplomatic Conference in 2013 to support developing countries and to promote voices and messages from Minamata. |
| NAP | National action plan |
| NIMD | National Institute for Minamata Disease |
| NOEL | No-observed-effect level |
| NOx | Nitrogen oxides |
| OECC | Overseas Environmental Cooperation Center |
| PDCA | Plan, do, check and action |
| PE | Polyethylene |
| PP | Polypropylene |
| PTWI | Provisional tolerable weekly intake |
| QA | Quality assurance |
| QC | Quality control |
| QMS | Quality management system |
| RM | Reference material |
| ROAP | Regional Office for Asia and the Pacific |
| SAICM | Strategic Approach to International Chemicals Management |
| SMSA | Standard metropolitan statistical area |
| S/N | Signal/Noise |
| SOP | Standard operating procedure |
| SOx | Sulphuric oxides |
| UN | United Nations |
| UNEP | United Nations Environment Programme |
| UNITAR | United Nations Institute for Training and Research |
| UPC | University of South Pacific |
| USEPA | United States of America, Environmental Protection Agency |
| USFDA | United States of America, Food and Drug Administration |
| UV | Ultraviolet |
| WHO | World Health Organization |
| wt | Weight |
| ww | Wet weight |
| XRF | X-ray fluorescence analyser |

# 5 EDITABLE POWERPOINT FILES

This Chapter provides the reading scripts of pre-recorded narration embedded in the multi-media files.

## 5.1 List of slide decks

*Lecture 1: Physical and chemical properties, usage, and environmental behaviour (29 slides, 24’58”)*

- Section 1: Physical and chemical properties of mercury (4 slides, 3’32”)
- Section 2: Mercury products and uses (3 slides, 1’55”)
- Section 3: Use of elemental mercury (5 slides, 4’47”)
- Section 4: Use of amalgam (5 slides, 4’26”)
- Section 5: Use of mercury compounds (8 slides, 7’43”)
- Section 6: The global mercury cycle and emissions (3 slides, 2’16”)

*Lecture 2: Atmospheric survey and analysis (manual active sampling method) (59 slides, 61’24”)*

Part I: Sample collection (33 slides, 35’01”)

- Section 1: Outlines of atmospheric mercury survey (4 slides, 5’40”)
- Section 2: Sampling equipment and its preparation (9 slides, 8’01”)
- Section 3: Atmospheric sample collection (12 slides, 10’39”)
- Section 4: Atmospheric surveys in special situation (7 slides, 10’30”)

Part II: measurement, data processing and QA/QC (25 slides, 26’09”)

- Section 1: Measurement of gold amalgamation cartridge (3 slides, 3’00”)
- Section 2: CVAAS measurement (6 slides, 8’06”)
- Section 3: Data processing and QA/QC (8 slides, 7’43”)
- Section 4: Maintenance and calibration methods (7 slides, 7’08”)

*Lecture 3: Solid sample (soil, sediment, and biota) survey and analysis (38 slides, 40’21”)*

- Section 1: Key characteristics of soil and sediment (3 slides, 3’00”)
- Section 2: Soil sample collection (5 slides, 5’57”)
- Section 3: Sediment sample collection (4 slides, 3’28”)
- Section 4: Biota sample (2 slides, 1’26”)
- Section 5: Total mercury analysis (9 slides, 9’23”)
- Section 6: Measurements, data processing, and QA/QC (9 slides, 9’36”)
- Section 7: Other methods for total mercury analysis (5 slides, 7’18”)

*Lecture 4: Water sample survey and analysis (30 slides, 28’02”)*

- Section 1: Key characteristics of water for mercury survey and analysis (3 slides, 4’03”)
- Section 2: Water sample collection (8 slides, 7’55”)
- Section 3: Total mercury analysis for water sample (14 slides, 12’02”)
- Section 4: Quality control - Reducing operation blank level (4 slides, 3’54”)

*Lecture 5: Human biological sample analysis (18 slides, 20’10”)*

- Section 1: Key characteristics of human biological samples (4 slides, 5’29”)
- Section 2: Hair sample collection (3 slides, 2’56”)
- Section 3: Total mercury analysis for human biological samples (10 slides, 11’15”)

*Lecture 6: Methylmercury analysis (15 slides, 11’27”)*

- Section 1: Key features of methylmercury surveys (4 slides, 3’22”)
- Section 2: Methylmercury analysis (7 slides, 5’38”)
- Section 3: Methylmercury analysis for human hair samples (3 slides, 2’10”)

*Lecture 7: Mercury monitoring and the Minamata Convention (24 slides, 18’28”)*

- Section 1: Outlines of the Minamata Convention (4 slides, 3’33”)
- Section 2: Measures to reduce mercury risks (8 slides, 7’09”)
- Section 3: Provisions facilitating the implementation of measures (4 slides, 3’09”)
- Section 4: Overall management of the Convention (3 slides, 1’32”)
- Section 5: Contribution of mercury monitoring to the Convention (4 slides, 2’50”)

*Lecture 8: Quality management (47 slides, 47’22”)*

- Section 1: Outline of TQM, QA, and QC (7 slides, 5’46”)
- Section 2: SOP and record: Process clarity (9 slides, 11’07”)
- Section 3: QA/QC analysis of samples: Result validity (9 slides, 13’13”)
- Section 4: Quality of data: Bias and uncertainty (6 slides, 5’14”)
- Section 5: Bias of data (3 slides, 1’34”)
- Section 6: Uncertainty (12 slides, 10’11”)

*Lecture 9: Laboratory safety and environmental management (23 slides, 21’49”)*

- Section 1: Safe laboratory operation (3 slides, 1’11”)
- Section 2: Safe handling of hazardous reagents (7 slides, 9’56”)
- Section 3: Apparatus and equipment safety (5 slides, 3’26”)
- Section 4: Environmental management (4 slides, 3’17”)
- Section 5: ISO 14001 environmental management standard (3 slides, 3’34”)

# 5.2 Lecture 1 Physical and chemical properties, usage, and environmental behaviour

‘0’ This lecture explains the basic scientific knowledge such as physical and chemical properties, usage, and environmental behaviour of mercury, which will help in understanding mercury issues.

*Section 1: Physical and chemical properties of mercury*

‘1’ This section explains the physical and chemical properties of mercury.

‘2’ Mercury is a chemical element that exists in various forms. With an atomic number of 80, which is next to gold, mercury is the only metal element that exists in liquid form at normal temperatures. In addition, mercury has a low boiling point among metallic elements, and it is volatile with a high vapour pressure. The abundance of mercury in Earth’s crust is similar to that of silver, but mercury has a much lower market price than precious metals.

‘3’ Methylmercury is a mercury compound of great concern due to its high toxicity. Methylmercury binds to cysteine, a kind of amino acid, to form a complex with a molecular structure similar to methionine, an essential amino acid. Due to this similarity, the complex is actively absorbed via an amino acid transporter. Then, it is incorporated into body tissues made of protein, including the brain and fetus.

‘4’ Most mercury and mercury compounds have certain toxicities, but their biological behaviours and toxicity levels differ. The absorption rates of inhaled elementary mercury and ingested methylmercury are very high, while the absorption rate of inorganic mercury is rather low. Ingested elemental mercury is usually directly excreted without absorption. Absorbed mercury is gradually oxidized and excreted in urine as inorganic mercury. Elemental mercury passes through the blood-brain barrier and causes mercury poisoning of the central nervous system. Accidental high-level exposure to mercury vapour in the workplace can be fatal, but acute symptoms are usually reversible. The symptoms of chronic low-level exposure to elemental mercury were known as mad hatter’s disease. Methylmercury is transported actively to form body tissues made of protein. The adverse effects depend on the body parts into which methylmercury is incorporated. Ingested inorganic mercury causes inflammation of the digestive tract and kidney damages if the amount is very high. Acute mercury exposure is usually treated by stimulating excretion. For chronic exposure, stopping the exposure is the most important measure.

### *Section 2: Mercury products and uses*

‘5’ This section provides an overview of various applications where mercury is found in products or processes.

‘6’ Mercury is one of a few elements known since ancient times. It has been used for various purposes for many thousands of years. Red pigments and the preservation of corpses are among the oldest applications. The demand for mercury has increased as new uses have been invented over time. The supply side, that is, mercury mining, has also been well developed to support the demand for mercury. Today, some mercury-added products and processes have been replaced by non-mercury alternatives, but many are still widely used globally. The Minamata Convention controls the products and processes stipulated in the Annexes, but even after phase out, mercury waste will continue to be generated for a long time. Thus, proper management of mercury waste is very important.

‘7’ Global mercury use is estimated to be approximately 4700 tons per year as of 2015. Artisanal and small-scale gold mining is the largest mercury consumer, and Asia, Africa, Latin America and the Caribbean are the regions consuming a large amount of mercury.

### *Section 3: Use of elemental mercury*

‘8’ This section explains the applications of elemental mercury in products.

‘9’ Elemental mercury is used for measuring purposes. As a high-density liquid, it is suitable for measuring pressure. Devices such as manometers, barometers, and sphygmomanometers enable precise pressure measurements without using electricity. For official purposes, mmHg or inHg can still be used as non-SI units of measurement. Mercury is also useful for measuring temperature because it exists in liquid form in a wide temperature range. As a metallic element, mercury has a high thermal conductivity, which provides a quick response. These mercury-added measuring devices are subject to phase out under the Minamata Convention.

‘10’ A discharge tube is an electronic device that contains gas or vapour at low pressure, and through which conduction takes place when a high voltage is applied. The mercury arc rectifier was an important device for converting high voltage alternating current, AC, to direct current, DC. As modern electricity supply networks were developed with AC, rectification was required if the industry required DC. Today, this function is mostly performed by power semiconductors. Several gaseous elements, including mercury vapour, emit various wavelengths of light. Mercury discharges ultraviolet ray, UV-C, which is invisible to humans. As UV-C damages DNA, mercury vapour lamps are used for microbial disinfection. Fluorescent lamps convert UV-C to visible light for lighting applications. The light emitted from discharge tubes is also used for various lighting applications, such as indoor and outdoor lighting, signage, and the headlamps of vehicles.

‘11’ As mercury is electrically conductive, it is used for various electric controls. The mercury switch has several advantages for closing and opening electrical circuits. As the contact surface is concealed, no oxidation occurs, and the surface remains clean with a low resistance due to the wetting nature of mercury. Application includes tilt switches to activate lights on the boot lids of vehicles, rollover warning devices for vending machines, anti-lock braking systems that detects acceleration force, high-speed switches as mercury relay does not cause chattering, and mercury slip rings that transmit signals or power to devices over 360° of rotation. Mercury is added to batteries for safety purposes to prevent hydrogen gas generation. Abnormal reactions at the zinc anode causes cell rupture or leakage, but mercury inhibits such abnormal reactions. Although most dry cells have stopped using mercury, a few types of button cells still use mercury for this purpose. Lithium coin cells do not use water as the electrolyte, so no mercury is added.

‘12’ Elemental mercury is also used for many other purposes. Some are being phased out as non-mercury alternatives are becoming increasingly available. It is important to be aware that not all uses of mercury are subject to the Minamata Convention, so legitimate uses of mercury will remain.

### *Section 4: Use of amalgam*

‘13’ This section explains the applications of amalgam in products or processes.

‘14’ Mercury can form various alloys with other metals, which are called amalgam. Amalgam has been an important material for many industries as final products or in production processes. Dental amalgam is a mixture of silver and tin powder, which is gradually hardened to fill dental cavities. Tin amalgam was used for the reflective surfaces of mirrors.

‘15’ Gold and silver extraction and refining have been practised for many thousands of years. The oldest method called cupellation used lead and was invented in the BC era. There was a risk for lead poisoning with this method. The amalgamation method was then invented in the 16th century, when silver mining in Latin America was at its peak. Due to the melting and boiling points of mercury being lower than those of lead, the consumption of heat sources, such as firewood, was reduced, which preserved forests in the region. The amalgamation method for ASGM accounts for the largest usage of mercury today and disproportionally affects marginalised and less privileged groups. The cyanide method was invented in the 19th century during the Gold Rush era. This method is currently predominantly used for large-scale gold mining operations, but its application to ASGM is being explored.

‘16’ NaCl, which is the chemical form of edible salt, can generate chlorine gas and caustic soda by electrolysis. Caustic soda is used for manufacturing products such as soap and glass, and chlorine gas is used for producing disinfection and bleaching agents as well as PVC. Mercury is used as the electrode for the mercury-cell process, which was invented in the early 20th century and is still used in some countries. Chlorine ions are oxidized at the anode and become chlorine gas. On the cathode side, where mercury is used, sodium ions are reduced to metallic sodium, which forms an amalgam with mercury. The sodium amalgam is then sent to an amalgam decomposer, where caustic soda is formed. The key to this electrolysis process is blocking sodium backflow to the anode side. The diaphragm process physically blocks this backflow with the fibrinous structure of asbestos. This system is still used, but the risk of asbestos is a concern. The membrane process has a similar configuration to the diaphragm process, but an ion exchange membrane allows the selective permeation of sodium ions to the cathode side, which is more energy efficient and avoids toxic substances.

‘17’ Special applications of amalgam includes low-temperature thermometers with thallium amalgam, which is a melting temperature of approximately minus 60 °C. However, mercury is problematic in the oil and gas sector. Mercury erodes aluminium equipment, such as heat exchangers, and inactivates palladium-based catalysts.

### *Section 5: Use of mercury compounds*

‘18’ This section explains the applications of mercury compounds in products or processes.

‘19’ Mercury sulphide is naturally found as cinnabar, which exists as blood red crystals or dark red stones. Red is one of the oldest colours that humans have intentionally used since the pre-historic era. Three major red pigments have been used. Iron oxide provides brownish red and is easily available from red clay soil. By contract, mercury sulphide needs laborious refinement from ore, so it was an expensive pigment. It can also be synthesized from mercury and sulphur. Due to its preciousness, mercury sulphide was used for more important occasions, such as ceremonial and religious purposes. Lead oxide is also a synthesized pigment with a bright orange colour.

‘20’ Cosmetics also use colour, which are predominantly consumed by women. Red, white, and black are the three base colours for cosmetics. Red pigments, such as cinnabar, were used for bodypainting in some indigenous societies. More broadly, white face powder has been used for makeup. Calomel, mercury (I) chloride, is a white powder used for such purposes. Other chemicals, including lead white and talc, have also been used. Lead poisoning by face powder was problematic in the past few centuries. Currently, concerns have been raised about talc, which contains asbestos as an impurity. Mercury use for skin-whitening cream is another concern, as it is still widely used globally. The preference to lighter coloured skin is still prevalent in many countries where the skin care industry keeps feeding illegal products into market.

‘21’ The biocidal action of mercury is used for fungicides and preservatives. Organic mercury compounds such as phenylmercury have been used for seed dressing, as fungicides for crops such as rice and wheat. Among inorganic mercury compounds, mercury chloride has been used for wood preservation and red mercury oxide has been used for anti-fouling ship paint. In some products that are directly applied to humans, mercury compounds are still used as preserving agents. For example, thiomersal preserves vaccines at normal temperatures, which is important when providing vaccines to remote areas where no cold chain is available.

‘22’ Mercury has been used in pharmaceuticals since ancient times. Traditional Chinese and Ayurveda medicines still include mercury products. One of the most significant historical uses of mercury for pharmaceutical purposes is the treatment of syphilis patients. Syphilis emerged in the late 15th century and rapidly spread over the globe. Many types of mercury compounds were used for medical treatment from the 16th century until being replaced by penicillin in the 1940s. Mercurochrome is a water solution of the organic mercury compound merbromin, which was invented in the early 20th century and has been widely used for treating minor wounds. Its less painful nature and cheap price allowed various applications in both clinical and household settings. Mercury inhibits the growth of microorganisms. This characteristic has been used for many preservation and antiseptic purposes.

‘23’ A catalyst is a substance that facilitate or accelerates a chemical reaction, but its form remains unchanged. The elements in the zinc group, which includes mercury, have been used as catalysts for organic synthesis, particularly for the production of vinyl polymers by accelerating addition reactions from acetylene. The catalysts form intermediate compounds to promote addition reactions. Minamata disease was caused by the mercury catalyst used for acetaldehyde production, which was methylated in the factory and then released into the environment. To avoid the use of mercury, ethylene can be used for the feedstock instead of acetylene. Another type of catalyst is the initiator for polymerising polyurethane elastomer, which triggers the process in moulded products or coatings. Although mercury acts as a catalyst for this process, it remains in the final product.

‘24’ Batteries, especially chemical batteries, utilize the oxidation and reduction of chemical compounds to store electricity. The mercury cell is a type of battery that has a mercury oxide cathode. Once electricity is consumed, mercury oxide is reduced to metallic mercury, which flows out of the cathode. This product is subject to phase out under the Convention. However, mercury use for research, calibration, and reference is exempt from the Convention, so standard cells such as the Weston cell are not subject to phase out.

‘25’ Various mercury compounds are used for many other purposes. One of historical uses is mercury (II) nitrate for hat making. A process called ‘carroting’ was extensively used for the preparation of felt. Mercury (II) fulminate was also an important mercury compound used extensively during wars as a material for the detonation caps of explosives. A new use has been examined for mercury (II) sulphide for the final disposal of mercury waste because stabilisation is required in some countries to dispose of mercury.

## *Section 6: The global mercury cycle and emissions*

‘26’ This section explains the global mercury cycle and emissions.

‘27’ As a chemical element, mercury has existed on Earth since its creation. Mercury is released from natural sources by processes such as volcanic activity and permafrost melting. Once released, mercury poses risks to human health and the environment. In recent years, more mercury has been released through human activities, such as the combustion of fuels, mining activities, and the consumption of mercury-added products. Mercury emitted to the atmosphere remains for a long time and will be transported long distances. Atmospheric mercury is gradually oxidized and deposited in the ocean or on land. Inorganic mercury in water bodies can be methylated by microbial activity and bioaccumulated in biota at higher trophic levels. Eventually, fishing brings mercury back to human society through consumption.

‘28’ Similar to mercury usage, the largest mercury emission source is ASGM, which disproportionally affects marginalised and less privileged groups, such as children and women of child-bearing age. Asia, Africa, and Latin America and the Caribbeans are the regions emitting large amounts of mercury. The burning of fossil fuel and the production of cement and non-ferrous metals all remove mercury from the soil and emit it into the atmosphere. More importantly, such mercury by-product might increase with the economic development of developing countries.

# 5.3 Lecture 2 Atmospheric survey and analysis (manual active sampling method)

‘0’ This lecture discusses atmospheric survey and analysis particularly the manual active sampling method using gold amalgam trap cartridge.

**Part I: Sample collection**

‘1’ This part describes sample collection for the manual active sampling method of atmospheric mercury monitoring.

*Section 1: Outlines of atmospheric mercury survey*

‘2’ This section explains three methods that are often used in atmospheric mercury monitoring.

‘3’ This slide shows the survey scene using the three survey methods for atmospheric mercury monitoring. Atmospheric mercury survey methods are subdivided into the following three methods depending on how mercury is collected and measured. They are automated active sampling method, manual active sampling method, and passive sampling method.

In the automated active sampling method, mercury in the atmosphere is automatically collected and measured by a dedicated device that continues to measure mercury at regular intervals. The advantages of this method are the ability of continuous monitoring in a very short cycle to get real time data continuously. The equipment is commercially available and can speciate mercury into three types depending on physiochemical properties, namely, elemental mercury, oxidized mercury, and particle-bound mercury. However, the equipment is expensive, and the operation requires sufficient skills and experiences.

In the manual active sampling method, the collection material and air pump are brought to the survey sites. Mercury is adsorbed on to the collection material on site, and then the analysis is performed in the laboratory. This method can monitor mercury with a very small, lightweight, and inexpensive device. The sampling time, which is the survey interval, is longer than that of the automated active sampling method, but shorter than the passive sampling. It is often approximately 24 hours for ambient monitoring.

In the passive sampling method, mercury is collected using a passive sampler that adsorbs mercury in the atmosphere naturally without using a pump or other devices and it follow diffusion process in atmosphere through sulphur coated charcoal. After collection, analysis is performed in the laboratory in the same way as in the manual active sampling method. It is very easy to install samplers on site, which makes simultaneous surveys of a large number of points possible. The sampling period is often several weeks to one month, which is longer than those of the other two methods as it is less time sensitive.

Each of these methods has its own strengths and weaknesses, so it is necessary to use a method that is suitable for the purpose of the survey.

‘4’ The manual active sampling method is outlined, and the tools and devices used for this method are explained. This explanation is based on the manual active sampling method used for hazardous air pollutant survey in Japan, which uses gold-coated particles as a mercury trap. The manual active sampling method can be introduced with relatively inexpensive devices and less training. Besides that, because it is easy to handle, it can be applied in many sampling locations.

‘5’ This is a schematic diagram of the collection system for atmospheric mercury by manual active sampling method. It is configured with a gold amalgamation cartridge, a pump to draw air, a soda lime trap to filter out interferents, and connecting pipes. The principle is simple: the gold amalgamation cartridge is used as an adsorbent, and air is sucked by the pump to be fed through the adsorbent. When the air passes through the adsorbent, mercury in the air forms an amalgam with gold in the adsorbent and is taken up by the adsorbent. The mercury collected as gold amalgam is very stable and can be easily transported and stored at room temperature. This mercury can then be extracted by heating the adsorbent. In the laboratory, the mercury expelled by heating the adsorbent is introduced into an analytical instrument for measurement. Gold cartridges that have been analysed can be reused for another survey.

### *Section 2: Sampling equipment and its preparation*

‘6’ This section provides an overview of the equipment used for sample collection and the operations for its preparation.

‘7’ This slide shows the equipment required to collect samples for mercury in air using the manual active sampling method. The equipment required includes gold amalgamation trap cartridges, trap tubes filled with soda lime, air pumps, tubes, and pipes. A thermometer, hygrometer and barometer are also useful when making temperature and pressure corrections to the volume of air sucked.

‘8’ Firstly, the gold amalgamation trap, which is the adsorbent, is described. The adsorbent in the surveys consists of particles with gold coated on their surfaces contained in a quartz tube with an inner diameter of four mm. The collection capacity of mercury in the air is quantitative in most cases. The adsorbent can be used repeatedly, so the operational cost is very low.

‘9’ This slide describes the preparation of gold trap cartridges prior to the survey. Needless to say, the gold cartridges used for the survey must be free from mercury. Mercury can be removed from the gold cartridges by heating, so the cartridges can be cleaned after they are analysed using an analytical instrument. However, once cleaned, the cartridges gradually absorb mercury from the atmosphere if they are left open. They should therefore be kept in a tightly sealed container during storage and transport. The same applies after the samples have been collected. Even if the sample is kept in a tightly sealed container, it could gradually absorb mercury over a long storage time. During transport and storage, the sample might be exposed to an environment with unexpectedly high mercury concentrations. It is therefore recommended that separate cartridges are prepared for field blank testing to evaluate the unintentional absorption of mercury.

‘10’ This is a soda lime trap for removing interfering substances. Moisture, halogens and nitrogen oxides present in air have an adverse effect on mercury analysis. The soda lime absorbs many of these substances and reduces the interference with the measurement.

‘11’ This slide shows the preparation of a soda lime trap. A short fluoropolymer pipe, just large enough to fit a gold cartridge, is prepared. One end of the pipe is filled with quartz wool, and then the pipe is filled with soda lime from the other end. Preparation is completed by filling the other end of the pipe with quartz wool. The amount of interfering substances that the soda lime can absorb depends on the environmental conditions and the soda lime used. As soda lime is a relatively inexpensive reagent, the soda lime trap should be replaced with a new one every time a sample is collected.

‘12’ This slide shows an example of a pump that is commonly used in the manual active sampling methods. Most air suction pumps can be used, as long as they draw air stably. The gold cartridge method uses a flow rate of approximately 0.5 litres per minute, which means that even a very small pump is sufficient. The low power consumption also means that many pumps can be run on battery power alone, without an external power supply. In addition to the pump, a flow integrator is required to record the flow rate. If using volumetric flow controllers, the temperature and pressure must be recorded separately to convert the flow rate to standard conditions. This is unnecessary with mass flow controllers, as the conversion is done automatically. Some pumps are equipped with a mass flow controller, which allows the survey to be carried out in a very small space. However, pumps are usually not waterproof and do not operate properly at extremely high or low temperature. For this reason, they must be stored in a shelter or case during the survey.

‘13’ The tubes connecting the gold cartridge to the pump should be clean, free of holes and cracks, and able to connect devices without air leakage. As the tube is connected to the leeward side of the adsorbent, the air that passes through the tubing does not enter the adsorbent. Thus, various materials other than glass or fluoropolymer can be used. It is sufficient to prepare the tube by rinsing with clean water, drying, and storing in a plastic bag to prevent dusts. It is not necessary to clean the tube with acids.

‘14’ The picture on this slide shows a small multi-functional data logger that can measure and record temperature, humidity and barometric pressure, which is suitable for survey sites. If the sampling flow is measured with a mass flow controller, the temperature and pressure at the time of the survey are not absolutely necessary, but they still provide important information for understanding the conditions at the time of the survey. It is helpful if a meteorological facility is in the vicinity of the site and the data is available. If not, it is necessary to install thermometers and barometers at the sampling site. As shown in this photo, small loggers are available on the market that can measure temperature, humidity and pressure and record this information at regular intervals in their internal memory.

### *Section 3: Atmospheric sample collection*

‘15’ The actual collection of atmospheric samples is explained in this section.

‘16’ If the purpose of the air quality survey is to understand the general conditions in the area, it is important to select a representative site. A location with no emission sources of mercury in the immediate vicinity and where there are no special airflow patterns due to buildings or topography should be selected. Different criterial will apply if the influence of sources is to be investigated.

‘17’ Prior to setting up the gold cartridges and other survey equipment, the survey site should be prepared. In areas where the ground is bare soil or there is a lot of dust, covering the site with a sheet is desirable to prevent adverse effect from roll-up dust. A shelter to protect the pumps from rain and direct sunlight is also necessary. A small tent will suffice for the purpose. It is also possible to use a container with a fan for heat removal.

‘18’ This slide shows the stand posts and pipes for supporting gold cartridges. The position of the gold cartridges should not be too low, to avoid influence from the ground surface. The monitoring manual indicates a minimum height of 1.5 metres, which often requires the use of a stand to hold the cartridge. It is advisable to insert the gold cartridge into a pipe that is slightly larger than itself for protection from rain and dust during sampling. Many materials can be used, including plastics such as PVC pipes, which are the easiest choice for this purpose.

‘19’ The procedure for setting up the equipment for sample collection is described. The first step is to prepare the air pump and tubing. The tube is fixed along the support and connected to the pump. The functions of the pump are checked before sampling to ensure that the pump is working properly and the flow rate is set correctly. Most surveys are carried out at a flow rate of approximately 0.5 litres per minute.

‘20’ Once the support and pumps are set properly, the gold cartridges are installed. Gloves should always be worn when handling the gold cartridge. Disposable gloves are useful for this purpose. If field blanks are being collected, the case is opened together with the gold cartridges for sampling. Then, the gold cartridge is taken from the container and connected to the soda lime trap. The flow direction indicated on the cartridge should be confirmed when fitting the cartridges to the tubes. The gold cartridge connected to the tube is inserted into the protective pipe. Ideally, the cartridge should be placed at an upright angle, but this may risk rainwater entering through the protective pipe. For this reason, it is recommended that the upper side of the pipe is covered and that the pipe is tilted slightly. In this example, the piped are covered with aluminium foil.

‘21’ After connecting the gold cartridge, pump and tubing, they are rechecked before sampling. For example, it should be confirmed that the flow of the gold cartridges is oriented correctly, that the tubing is securely connected without any air leakage, and that the tubes are not damaged.

‘22’ Once all the joints are properly connected, the pumps are turned on and sampling is started. For some time after the start, the flow controllers are checked to confirm that sampling is taking place at the set flow rate. If field blanks are being collected, the container with the cartridges for the field blanks is closed when sampling starts.

‘23’ Once sampling has started, the detailed status of the survey should be recorded. To facilitate later reference, a record form should be prepared in advance and the information should be recorded in this format every time.

The following information should be recorded: the date and time that sampling started, the date and time that sampling ended, the location of the survey, the person carried out the survey, the sampling flow rate, and the total sampling amount.

The information mentioned now is mandatory. The weather conditions on the surveying day are also important information. The temperature and atmospheric pressure should also be recorded if available. The gold cartridges and pumps are marked with unique ID numbers, which should be recorded at the time of the survey to track the status of the survey. It is also recommended that the record form includes a column for recording any special circumstances noticed during the survey. Such notes should be taken on site, unless prevented by weather conditions or other circumstances.

‘24’ This slide discusses inspections during sampling. As atmospheric mercury surveys take a long time and the investigator is usually not present at the site most of the time, it is useful to check the operating conditions during the sampling period if circumstances permit. It is recommended that the sampling site is revisited during the sampling period to check items including if the sample collection is being carried out correctly, if any problems such as stands falling over or tubes disconnecting has occurred, and if the sampling flow rate is correct. It is useful to have the space to note the check results in the record form.

‘25’ When the sampling time is over and the required amount of air has been collected, the sampling equipment is retrieved. Surveys are typically carried out over a 24-hour period. Firstly, the equipment is examined to ensure that the survey has been carried out properly. Next, the pump is stopped, and the final sampling volume is recorded. If field blanks are being collected, the case should then be opened. The dismantling operation should be performed using the following procedure. Gloves should always be worn during this process, as was done during installation. The tubing and soda lime trap are removed from the gold cartridges and placed in the case. The case of the field blank cartridges is closed when the samples cartridges are stored in the container. Then, other devices such as stands, shelters, and sheets, are collected. When the cartridges are sent to the laboratory for analysis, high temperature and strong light should be avoided during transportation.

‘26’ Duplicate sampling is used to confirm the stability of the survey. It is recommended that duplicate sampling is carried out at regular survey intervals such as one duplicate for every 10 sampling operations. The procedure is simply to deploy two or more gold cartridges side by side. If each of the sampled duplicates shows a similar concentration of mercury, then the influence of the survey equipment on the result is not significant.

### *Section 4: Atmospheric surveys in special situation*

‘27’ Atmospheric mercury survey and monitoring is not limited to the general environment. There are situations where mercury survey or monitoring is required for other purposes. In many cases, the manual active sampling method is useful. This section provides examples of such situations.

‘28’ This slide shows examples of survey or monitoring situations in non-general environments. Some precautions for dealing with issues in special situations for atmospheric mercury survey and monitoring are explained. When a high atmospheric mercury concentration is expected, the survey should be conducted with due concern for protecting the workers and nearby residents. Such special situations may occur in various scenarios. Firstly, compared to the general environment, higher mercury concentrations may be detected in the surroundings of mercury-using industrial processes or mercury-emitting facilities. Secondly, high mercury concentrations may be detected in working environments where mercury is used, such as artisanal and small-scale gold mining sites. High atmospheric mercury concentrations may also be detected at waste dumping site where the illegal or improper dumping of mercury-added products is found. Atmospheric mercury should also be surveyed in the event of an accident involving mercury or mercury products although continuous monitoring may not be necessary. For example, an accidental leakage of metallic mercury, or a fire at a facility using mercury requires a quick response to assess the impact on the residents of the surrounding area. In these situations, especially where mercury or mercury products are present, the atmospheric mercury concentration may be of the order of thousands of times higher than that of the general environment.

‘29’ Besides general environmental monitoring, temporary survey may be conducted rather than periodic monitoring. The manual active sampling method has advantages for temporary surveys as the sampling equipment is small and easy to carry. Set-up can usually be completed in one hour and only requires a small space. Additionally, the battery-run pumps require no external power supply. If the objective of the survey is to obtain the mean concentration level, the required sampling time may not be long. Normally, atmospheric samples are collected for 24 hours, but the sampling time may be shortened to one hour if the concentration is very high and a highly sensitive instrument, such as a cold vapour atomic fluorescence spectrometer, is used for mercury detection. However, some precautions should be kept in mind when using this manual sampling method in such situations, including the adverse effect of high mercury concentrations, and the presence of interfering substances during analysis.

‘30’ In cases of gold mining workplaces using mercury and accidental spill or leakage sites, the atmospheric mercury concentration may be especially high, of the order of thousands of times higher than that of the general environment. Since analytical instruments have upper limits, mercury samples with high concentrations cannot be measured. Additionally, samples with high mercury concentrations, that exceed the maximum value of the calibration curve should not be analysed.

‘31’ Some precautions and measures should be taken for surveys in environments with high atmospheric mercury concentrations. Firstly, the upper limit of the analytical instrument should be confirmed. The sample volume is determined based on the expected concentration and the instrumental upper limit. The sample volume should be smaller than that of the general environment; thus, reducing the flow rate is a good way to reduce the sample volume. The degree of reduction depends on the performance of the pump and flow controller. According to the Japanese manual, the flow rate should be more than 0.1 litres per minute because the flow rate of many types of pumps become unstable below that level. Shortening the sampling time is another way to reduce the sampling volume. If using this option, the daily average cannot be obtained. This precaution should be kept in mind for surveys where diurnal variation is large, such as in workplaces. Even when the mercury amount in the sample is within the measurement range of the instrument, it cannot be analysed if the value is outside the range of the calibration curve. Thus, a standard at a higher concentration should also be measured to create the calibration curve if a high concentration is expected. It is also important to note that the atmospheric sample cannot be diluted after sampling. This is a major difference from other media such as water, soil, and biota, where samples can be analysed again with smaller sample volumes using the remaining sample. Atmospheric samples should be measured all at once using the entire sampling volume. Therefore, if the mercury concentration in the sample exceeds the upper limit of the instrument, it cannot be analysed. In such cases, the sample should be collected again with a smaller sampling volume. If the mercury concentration level of the survey area is unknown, multiple samples with different sampling volumes should be collected.

‘32’ Interfering substances for instrumental measurements sometimes exist in large quantities, especially in factories or workplaces. Aerosols, including smoke, restrict the performance of mercury collection, causing damage to the cartridges. The effect of aerosols is negligible in the general environment, but a filter may be required in locations such as fields with open burning, where high aerosol levels are present. Some chemical substances may also affect the instrumental measurement data. Examples include halogenated gases such as chlorine and hydrochloride gas, nitrogen oxide and sulphur oxide, and gaseous organic compounds. The measurement data can also be affected by very high humidity and, in very rare cases, a high concentration of ozone. In the general environment, halogenated gases, NOx, SOx and moisture can be removed by the soda lime trap, and most other substances pass through the gold cartridge. However, in environments with especially high concentrations, such interfering substances may remain on the gold cartridge and affect the analysis data.

‘33’ There are some measures that can be taken against high amounts of interfering substances. To remove a high amount of aerosol effectively, a filter can be attached in front of the cartridge. To remove gaseous interfering substances, such as halogenated gases, NOx, and SOx, a larger soda lime trap may be sufficient if the amounts of these substances are not extremely high. If the amounts are much higher, a gas scrubber is effective. When a gas scrubber is used, it should be attached in front of the soda lime trap as it generates water mist. If the electrical power supply is accessible, a heater can be attached to the gold cartridge to maintain the temperature in the range from 100 to 150 degrees C. Although this is a relatively complex method that requires a heater and temperature controllers, heating the cartridge is very effective for removing interfering substances.

## **Part II: Measurement, data processing and QA/QC**

‘34’ This part describes the analysis of the mercury adsorbed by gold cartridges, data processing, and quality control.

### *Section 1: Measurement of gold amalgamation cartridge*

‘35’ This section outlines the operation of a thermal desorption atomic absorption spectrophotometer, which is the analytical instrument used for atmospheric samples.

‘36’ This slide shows a conceptual diagram of the instrument used for analysing gold cartridges. Gold cartridges selectively adsorb mercury in the atmosphere, allowing many interfering substances to pass through. However, some interfering substances are adsorbed by the cartridge, which may affect the analysis. To prevent adverse effects from interfering substances, this instrument applies the double amalgamation method, which uses two gold cartridges. A cartridge that collects atmospheric mercury is installed, as shown on the left side of the drawing. The device is also equipped with another cartridge, through which the collected mercury is introduced into the atomic absorption spectrophotometer. The carrier gas used to deliver mercury must not contain mercury. This instrument uses additional gold cartridge as a mercury scrubber to obtain mercury-free air. Thus, mercury-free air can be supplied to the atomic absorption spectrophotometer in a very simple and inexpensive way.

‘37’ This slide explains the flow of analysis for mercury collected in a gold cartridge. Firstly, air passes through the system from the first cartridge, which contains mercury collected in the atmosphere, and then the second cartridge, which is connected to the analytical instrument. Next, the first cartridge containing sampled mercury is heated to purge the mercury. When the cartridge is heated, the collected mercury flows to the second cartridge and is adsorbed. However, most of the interfering substances adsorbed in the first cartridge pass through the second cartridge. This process leaves only mercury in the second cartridge and removes most of the interfering substances. Finally, the second cartridge is heated, and mercury is introduced into the atomic absorption spectrophotometer for analysis. This device consumes almost no reagents or gases.

*Section 2: CVAAS measurement*

‘38’ In this section, the instrumental analysis is described. The key points for sample analysis as well as the analyses required for quality assurance, QA, and quality control, QC are discussed. The operation Details differ for each analytical instrument and thus will not be covered here.

‘39’ This video shows the analysis of gold cartridges with an atomic absorption spectrophotometer. In many instruments of this type, a cartridge that collects air must be installed at a particular port in addition to another cartridge that act as a mercury scrubber. Once the instrument is switched on, the double amalgamation process runs automatically, and mercury analysis is performed. In addition to the cartridge containing the collected sample, a blank cartridge that does not contain mercury or standards for calculating the mercury concentration must also be analysed. If there are many samples to analyse, it is necessary to measure the checking standards every 10 samples to check the sensitivity of the instrument. For this, a standard with a moderate concentration, that is, a standard from the middle of the calibration curve, is used.

‘40’ The preparation of the standard for atmospheric mercury analysis is explained here. Since the atomic absorption spectrophotometer relies on comparative analysis, it is necessary to analyse a mercury standard to determine the absolute mercury concentration using this instrument. A commonly used method is to collect a certain amount of saturated mercury vapour and introduce it into the analytical instrument. This slide shows a conceptual diagram of such a mercury standard gas generator. Metallic mercury is contained in a closed chamber, which is saturated with mercury vapour. The temperature in the chamber is measured with a thermometer, and then the mercury concentration in the chamber can be calculated. When a certain amount of air in this chamber is collected with a gas tight syringe, the amount of mercury collected can be calculated from the volume of air collected and the saturated mercury concentration. Then, the saturated mercury vapour is injected into the instrument to analyse the known amount of mercury. Mercury gas generators that combine such a closed chamber and a thermometer are commercially available, and by using these devices, it is possible to prepare a mercury standard for creating a calibration curve.

‘41’ This slide describes the procedure for introducing mercury vapour into the instrument. All that is required is a mercury gas generator, a gas tight syringe, and an atomic absorption spectrophotometer. Additionally, a comparison table between the temperature and saturated mercury concentration should be prepared to determine the gas level in the chamber when drawing it into the syringe. Such comparison tables are available on several websites. Firstly, the temperature inside the closed chamber is confirmed and recorded. Then, the saturated mercury concentration to be drawn from the chamber is recorded by using the comparison table. After that, the gas-tight syringe is inserted into the injection port of the mercury gas generator and a certain amount of mercury gas is drawn. Finally, the syringe is inserted into the injection port of the analytical instrument and the mercury gas is introduced. The amount of mercury is measured directly and recorded as standard data for the sample analysis.

‘42’ To develop a calibration curve, standard analysis is conducted at multiple concentrations by injecting different amounts of mercury gas. A calibration curve should include four or more concentration points, which means five or more samples should be used, including zero blanks. It is important to note that the collected atmospheric mercury sample can be analysed only once. If the mercury concentration is higher than expected and exceeds the range of the calibration curve, there is no other way to obtain data than collecting the sample again in the field. Therefore, it is recommended that the calibration curve range is set to a slightly higher level than the expected concentration and that the number of calibration curve points is increased, if necessary.

‘43’ There is an alternative methodology that does not use saturated mercury vapour from a standard gas generator. An inorganic mercury standard solution can be reduced to produce gaseous mercury. This slide shows a conceptual diagram of a device for generating mercury gas by reduction and vaporization. Firstly, a mercury standard solution with a mercury concentration corresponding to the calibration curve is placed in a sealable glass container such as a stoppered flask. Then, the system is assembled with a gold cartridge to remove mercury from the carrier air, a soda lime trap, a gold cartridge to adsorb mercury from the standard solution, and a pump. After assembly, a tin chloride solution is introduced into the flask. Then, the pump is turned on to let air flow through the system. Mercury in the solution is reduced and purged into the air, which is then sucked by the pump, and gaseous mercury is adsorbed by the gold cartridge. By repeating this operation several times, a set of gold cartridges with different concentrations is prepared, which provides the necessary concentration steps to create a calibration curve. Standard data is then obtained by analysing all these gold cartridges with an atomic absorption spectrophotometer.

### *Section 3: Data processing and QA/QC*

‘44’ After analysing the samples, the mercury concentrations of the samples are calculated based on the sample data and standard data. This section describes data processing and items used for QA/QC.

‘45’ Once the analysis data is available, the concentrations of the samples are calculated. This slide shows the formula for converting the analysis data from the atomic absorption spectrophotometer into the atmospheric concentration of a sample. A calibration curve is created from the standard data to calculate the amount of mercury in a collected samples. The concentration is calculated by dividing the amount of mercury obtained by the collected volume. As the concentration should be presented in standard conditions, it should be converted using the temperature and barometric pressure at the time of sampling, unless a mass flow controller was used for sampling. The standard conditions usually refer to zero °C and one atm, but monitoring results in Japan are converted to 20 °C and one atm.

‘46’ When analysing mercury, the operation blanks and field blanks, if collected, should also be analysed. Testing an operation blank is rather simple, as a gold cartridge that has been stored and has not been used for sampled or absorbing a standard gas is analysed. Normally, no noticeable blank value is detected, as long as the gold cartridge is stored properly. It is important to reiterate that the collected air samples can be analysed only once. Therefore, the analysis of the operation blank must be performed before analysing the collected samples. If a significant value is detected in the operation blank, the causes should be investigated and measures for resolving them should be taken before analysing the collected samples.

‘47’ It is recommended that a field blank, or travel blank, is performed approximately once in every 10 sampling operations. It is also recommended that three or more gold cartridges are used, instead of one, when investigating the field blank. The field blank usually does not show a high value in normal surveys, but the level can be elevated on some situations, such as surveys of mercury-using facilities, due to operational reasons.

‘48’ Even if the collected samples are exposed to a high concentration of mercury during the survey or transportation, the value of the field blank can be subtracted from the results by assuming that all cartridges have adsorbed the same amount of mercury. This judgment cannot be made with a single field blank. The effect on all collected samples can be estimated from the variation in the field blank value if multiple field blank samples are collected. When a large value is found, a field blank investigation with more than three samples will enable the contamination to be quantified by calculating the standard deviation. If the standard deviation of the field blank samples is smaller than the detection limit, the samples are considered uniformly contaminated, and the average value of the field blank samples can be subtracted from the analysed values of the collected sample.

‘49’ This slide describes duplicate sampling. To ensure the stability of the survey, it is recommended that duplicate sampling is performed at least once in every 10 survey operations. Two or more cartridges are used simultaneously for sample collection and the analytical results are compared. The values should be within 30 % of each other, but the difference is usually much smaller.

’50’ The limit of detection, LOD, and limit of quantification, LOQ, of the method should be confirmed prior to the survey. The LOD and LOQ of the method are obtained from the standard deviation for repeated analyses of low-concentration standard gas. Five or more standard gas cartridges, whose concentration is usually the minimum point of the calibration curve, are prepared and analysed. The LOD and LOQ are estimated from the standard deviation of the obtained results. The LOD is three times the standard deviation, and the LOQ is 10 times the standard deviation. These limits are defined by the amount of mercury detected, so the limits at actual concentrations will vary depending on the collected sample volume. For 24-hour sampling, these limits are significantly lower than the background atmospheric mercury levels, which has little effect on the survey results. This effect, however, must be taken into consideration when sampling is only performed for a short period of time, such as during indoor air surveys.

‘51’ It is important to mention that the survey data must be obtained in a usable manner. The obtained data should be compiled with ancillary information such as the date and time of the survey, the location of the survey, and the weather conditions at that time, to improve the usefulness. Electronic files with related data recorded by location, year, etc. are useful. It is more effective if a database system is created.

### *Section 4: Maintenance and calibration methods*

‘52’ In this section, maintenance and calibration methods for the QC of two pieces of equipment are explained.

‘53’ This slide explains the method for confirming the recovery rate of a gold cartridge. A gold amalgamation cartridge can be used repeatedly for atmospheric sample collection. However, the cartridge may be damaged and the mercury recovery rate may decrease if sampling is conducted under abnormal conditions where a large amount of aerosol is present. When such damage occurs to the gold amalgamation cartridge, signs are often found, such as lower concentrations than normal monitoring results or inconsistencies between duplicate samples. In these cases, the recovery rate of the cartridges should be confirmed.

The video shows the confirmation procedure for the recovery rate of a cartridge. Firstly, the cartridge is connected to an air pump. The pump used for sampling is suitable for the purpose. After the preparation of the cartridge and pump, mercury standard gas is drawn from the standard gas generator. The gas should be drawn from the same standard gas generator as used to create the calibration curve. Once the mercury standard gas is drawn from the generator, the pump is turned on. As soon as the pump flow rate stabilizes, the mercury gas is injected into the cartridge. Immediately after injection, another gold cartridge is connected to the injected cartridge to remove mercury from the inflow air. The mercury-free air is fed into the cartridge for two minutes to allow the injected mercury to be adsorbed by the gold trap.

‘54’ After aspiration for two minutes, the cartridge is collected and measured by CVAAS. The standards for creating the calibration curve are also measured. The recovery rate is calculated from the ratio of mercury added to the cartridge and the analysed mercury amount. If the calculated recovery rate is low, the cartridge requires further cleaning.

‘55’ If the recovery rate of the cartridge is low, it should be cleaned. This video shows the cleaning procedure using alcohol. For cleaning, methanol or ethanol and a clean cotton swab are used. Firstly, the exterior of the surface of the tube is wiped. Next, the interior is wiped with a cotton swab dipped in alcohol. After wiping both the interior and exterior of the tube, the interior is wiped using a new dry cotton swab to remove the remaining alcohol in the tube. The cleaned cartridge is then left at room temperature until completely dry.

‘56’ This slide shows another procedure for cleaning the damaged cartridge by heating in an electric furnace. A cartridge made of quartz will be damaged if heated in the presence of sodium or calcium. Thus, it should be washed well prior to heating. After washing the cartridge, it is placed on a dish that can endure strong heat, such as a large evaporating dish, which is then placed in an electric furnace and heated at 800 °C for 30 minutes. After leaving to cool to room temperature, the cartridge is collected and stored in a case. There is no guarantee that the cartridge is in good condition after this procedure; thus, the recovery rate should be reconfirmed.

‘57’ The atmospheric mercury concentration is calculated from the sample volume, so the flow meter used in sampling should be accurate. To maintain an accurate flow rate, it is recommended that periodic calibration is conducted by using a standard flow meter. The video shows the calibration procedure using a standard flow meter. Firstly, the flow meter to be calibrated is connected to a standard flow meter and a pump. The flow meter in this video is built into the pump as a flow controller. To stabilize the air flow, a buffer tank is connected between the flow meter and pump. To perform calibration under the same conditions as during actual sampling, a gold cartridge and soda lime trap are connected in front of the flow meter. After set-up, air is aspirated through the assembled gold cartridge, flow meter, buffer tank, and pump at the same flow rate as during sample collection. The flow meter is adjusted to match the flow rate indicated on the standard flow meter.

‘58’ After adjustment, the actual calibrated flow rate and its uncertainty should be confirmed. Under the same conditions, the flow rate indicated on the standard flow meter is collected multiple times at the same interval, for example, one minute. After recording the flow rates, the average flow rate is calculated as the calibration value of the flow meter. Additionally, the standard deviation is calculated as the uncertainty of the flow meter.

# 5.4 Lecture 3: Solid sample (soil, sediment, and biota) survey and analysis

‘0’ This lecture mainly explains the sampling and analysis of solid samples, such as soil, sediment, and biota.

*Section 1: Key characteristics of soil and sediment*

‘1’ Firstly, the characteristics of soil and sediment samples, and the sampling procedures are explained.

‘2’ Importantly, soil and sediment are media that comes into direct contact with animals and plants. They have a significant impact on local agricultural production and food chains. Additionally, they are often directly affected by high levels of pollution including the release of waste mercury. Highly contaminated areas often appear in very limited extents; thus, great care should be taken when surveying contaminated areas. In addition, mercury in soil and sediment undergoes very complex transport and reaction processes, such as oxidation, reduction, methylation and demethylation, deposition and re-release into the atmosphere. Therefore, deliberate assessment is required to understand mercury behaviours in areas that include soil and sediment.

‘3’ Solid samples are relatively easy to collect, transport, and store as compared to environmental water. Nevertheless, special care needs to be taken when transporting and storing samples containing mercury, as it may volatize over time unless it is in a stable form such as mercury sulphide. Soil and sediment are the media surveyed for global environmental studies and when local impact from mercury-using facilities is expected. Soil and sediment near mercury-using facilities may be affected by the release or leakage of mercury. In such situations, mercury concentrations can vary significantly within a very small area. For locations where direct mercury release is expected, the survey samples should be collected within the smallest extent possible. River sedimentation may be affected locally by the flow of the river, but it is not possible to know the overall sedimentation status of the entire river from one sediment sample. Thus, it is necessary to collect samples from multiple locations.

*Section 2: Soil sample collection*

‘4’ This section introduces composite sampling method using five soil core samples

‘5’ The soil sampling method should be selected considering the purpose of the survey, the condition of the survey site, and the issues to be evaluated such as the effect of mercury deposition in the background environment or the effect of leakage from a facility. Sometimes stratified deep core samples may be required or just shovelling soils may be sufficient. Five-point soil sampling is a method for surveying a relatively wide area with a relatively small number of samples. This method is suitable at locations where there is no directly released contamination or where the contamination from the polluting facility is sufficiently distant, so that little localised contamination is expected within the survey area. This method involves collecting samples from five adjacent points, which are then mixed in equal amounts to make one analytical sample. This method gives an assessment result for a wide area of soil environments at once.

‘6’ To conduct five-point sampling, the centre of the survey point is determined. Soil samples are collected at the centre and from four locations at equal distances to the north, south, east, and west. The distance between the points depends on the size of the survey area, with a distance of five to 10 meters often being chosen. Although it is better to maintain the same distance in all directions, it may be adjusted to some extent if some obstruction exists. The samples are cored from these five points.

‘7’ The image shows the core sampler used for soil sampling. This core sampler is driven into the soil from the surface to collect samples. The surface soil can also be collected with a shovel or other tools, but a core sampler is recommended because it collects the same volume of soil at each depth. This is especially relevant, as the mercury levels in soil could differ at different depths. Gloves should always be worn when collecting samples and handling the collected samples. Disposable gloves are convenient for this purpose. Firstly, the extraction handle is attached to the sampler, which is then set on the sampling location and driven into the ground. Once the sampler is inserted to a certain depth, it is extracted with the handle. Sometimes the sampler may not reach the depth due to a hard object, such as a rock, underneath. To avoid the core sampler being damaged, the sampling location can be slightly adjusted to avoid such hard ground.

‘8’ Together with sampling, information such as the sampling location, sampling date and time, and the operator collecting the samples should be recorded. Additionally, features of the collected samples that might affect the mercury contamination status should be recorded, if identified. The colour of the collected soil should be referenced to a standard soil colour book and recorded, which will be useful for later analysis. Although soil colour and mercury concentration do not have a direct relationship, the soil colour can be used to group soil samples with the same characteristics. It serves as useful information for estimating the extent of contamination, if identified. When sampling is completed, the collected samples in the samplers are placed in plastic bags and brought back to the laboratory. Short transportation of samples can be done at normal temperatures. If transportation takes a long time or the samples are stored for some time before analysis, the samples should be kept at a low temperature to avoid the volatilization on mercury. At the laboratory, the five collected samples are mixed in equal weights, not the full samples. Thorough mixing is necessary to achieve homogenization for analysis.

### *Section 3: Sediment sample collection*

‘9’ This section explains the collection of sediment samples.

‘10’ Normally, sediment samples cannot be collected with a shovel, instead special samplers are used for this purpose. The video shows a sediment sampler called an Ekman-Birge mud collector. This instrument is thrown into water with the collection flaps open. When the collector reaches the bottom, a weight is dropped as a messenger to close the flaps. Then, the collector holds the sediment when recovered. The sediment sampler can conveniently collect sediment samples by being thrown into water from ships or bridges. As there is another sediment sampling method, core sampling differs from this grab-type collection method. In core sampling, a columnar sample in obtained to analyse the vertical profile of the sediment layers.

‘11’ Firstly, the mud collector is lowered from a ship or bridge above the sampling point to the bottom of the water body with the sampling port facing downward. Once the mud collector hits the bottom, the tension in the hanging rope decreases. The rope is pulled up a little to take up the slack, and then the messenger is plummeted along the rope. After the messenger reaches the mud collector, the collector is slowly pulled up. If sediment is not held in the mud collector due to factors such as the landing angle or malfunction of the messenger, the same process is repeated to collect a sediment sample. Since the properties of sediment usually vary significantly at different sampling points, at least three samples are collected and mixed to make a representative sample of the survey site.

‘12’ Collected sediment is spread over a vat to observe the colour, odour, and other features. The colour should be referenced to a standard soil colour book and recorded as a Munsell number, as is done for soil. The collected sediment is thoroughly mixed and then placed in a sealed container to take back to the laboratory. As is done for soil, the sediment must be kept in cold conditions when the transport time is long, or the samples are stored until analysis. Information such as the date and time of sample collection, the sampling location, and the operator collecting the sample should be recorded on site. It is also recommended that the type of mud collector used for sampling, and the properties of the sediment are recorded.

### *Section 4: Biota sample*

‘13’ This section briefly addresses the collection of biota samples.

‘14’ The collection of biota samples varies significantly depending on the purpose of the survey, the species, the habitat of such species, etc., and thus is not presented here. The important point is to identify the target species to be collected without ambiguity. Even if the species is identified, the value of the analytical results will be minimal without supplementary information such as the body length and weight of each sample. In particular, the body length and weight of fish have a strong correlation with mercury concentration. Other information such as the date, time, and place of collection is also essential. The sex and age of the biota samples are also valuable, if available. For biota samples such as fish, muscle tissue is taken, homogenized, and analysed. The muscular part of the sample is cut with a knife and homogenized with the knife, or a kitchen blender.

### *Section 5: Total mercury analysis*

‘15’ The analysis of total mercury in the laboratory is described in this section. Among several methods for analysing total mercury, cold vapour atomic absorption spectrometry, CVAAS, is explained. In this method, samples are digested with acid, and then mercury in the solution is purged out by reduction aeration.

‘16’ This diagram shows the operational flow of the acid digestion-reduction aeration CVAAS analysis method. Firstly, a sample is decomposed with nitric acid, perchloric acid, and sulphuric acid in an open vessel. After digestion, mercury in the sample solution exists in a divalent oxidized form, which is highly soluble in water. Once mercury is reduced with tin chloride to elemental mercury, which has low water solubility, it is vaporized and introduced into the CVAAS for measurement.

‘17’ The reagents used in this method are shown here. Concentrated nitric acid and perchloric acid are mixed in equal volumes to prepare a one-to-one solution. Concentrated sulphuric acid without a mercury blank, which is available commercially, is used. Sodium hydroxide solution is prepared by dissolving the reagent in a small amount of water, which generates dissolution heat. The solution can be prepared more easily if water is added little by little to minimise the heat generated instead of adding the water all at once.

‘18’ The preparation of a methylmercury solution as a standard solution is described here. Prior to the analysis, a standard solution is prepared for creating a calibration curve. It is also possible to dilute and use a commercially available standard solution. However, please be mindful that the general mercury standard solution is in an inorganic form under acidic conditions with nitric acid, which is relatively unstable once diluted. L-cysteine should, therefore, be added to the diluting water of an inorganic mercury standard solution to prevent the change in concentration. The standard solutions with L-cysteine is stable for at least six months if it is kept in dark and cool condition. A methylmercury standard solution is recommended for calibration curve, if possible, even for total mercury analysis. A very stable standard stock solution can be prepared by accurately weighing methylmercury powder and dissolving it in toluene. The prepared methylmercury standard stock solution is kept in an airtight bottle and can be used for a long period of time if stored in the refrigerator.

‘19’ The methylmercury standard stock solution is a toluene solution, which cannot be used for standard solution measurement. Therefore, methylmercury is extracted with L-cysteine to prepare an aqueous solution of a methylmercury-cysteine complex. Precise amounts of L-cysteine aqueous solution and methylmercury toluene solution are mixed to extract methylmercury into the aqueous phase, which is then centrifuged to separate the toluene. Finally, the remaining toluene is removed from the aqueous solution to make a standard solution for analysis. This methylmercury-cysteine complex aqueous solution is not as stable as the toluene stock solution, so that it should be discarded and re-prepared after approximately one month.

‘20’ The actual analysis operation is explained here. Firstly, the sample is weighed and placed in a container for digestion. Every morning prior to sampling, the condition of the analytical balance is checked with weights or other means. The amount of sample may vary depending on the estimated mercury concentration in the sample. The maximum amount is approximately 0.5 gram for this method. The digestion container can be any receptacle that can resist heating with a strong acid, and that does not elute or adsorb mercury. In this video, volumetric flasks are used for digestion, as the shape is suitable for this purpose. To check the quality of the analysis, duplicate samples are added every 10 samples. If available, a certified reference material, which has the same or similar properties as the samples being analysed with a certified mercury concentration, can also be included to examine the validity of the analysis results.

‘21’ The standard solution of methylmercury cannot be directly analysed by CVAAS. It must undergo the same sample digestion process. The mercury solution is added to the digestion containers so that the amounts of mercury are appropriate for creating a calibration curve. A container without added mercury is also prepared to serve as an operation blank.

‘22’ The samples are placed in the digestion containers and decomposed with acid. A zeolite boiling stone is placed in each container with the sample, and then one mL of deionized water is added. After that, the digestion acid is added to the container. Firstly two mL of a one-to-one mixture of nitric acid and perchloric acid is added, followed by five mL of sulphuric acid. When there are many samples to be analysed, the dispensers shown in the video might be convenient. The samples with acid are heated and digested at 200 to 230 °C. If a hot plate is used as is in this video, the surface temperature may be different at different areas. In particular, when placing many samples on a hot plate, some areas may not reach a sufficiently high temperature. Therefore, it is recommended that the surface temperature is measured during operation to confirm that the temperature is high enough for digestion. After digesting for 30 minutes, the heating is stopped and the samples are left to cool to room temperature. Once the sample is sufficiently cool, the volume is adjusted to 50 mL, and this solution is used for analysis. The same process is also applied for the standard solutions for the calibration curve.

‘23’ As soon as digestion is conducted, the operation details should be recorded. The necessary information for this pre-treatment operation includes date and time, operator, sample amount, duration of digestion, and final preparation volume. It is beneficial if the record form is prepared in advance. A remark box in the form can be conveniently used to add any notes about special situations that occur during the operation.

### *Section 6: Measurements, data processing, and QA/QC*

‘24’ Analysis, data processing, and QA/QC of the samples after acid digestion by reduction aeration CVAAS are explained in this section.

‘25’ After acid digestion, the samples are analysed with reduction aeration CVAAS. Prior to the measurement operation, the reagents must be prepared. Tin chloride is usually used to reduce and vaporize mercury in the sample solutions. To prepare the tin chloride solution, tin chloride is dissolved in concentrated hydrochloric acid and then diluted with deionized water. A trace amount of mercury may be present in the tin chloride solution at a level that would affect the operation blank. Most mercury can be removed by purging with nitrogen gas for approximately 30 minutes.

‘26’ Once the digestion process is complete and the tin chloride solution is prepared, the samples and standard solutions are analysed with reduction aeration CVAAS. The detailed operation may differ in different instruments. The explanation here is for a process with a relatively simple instrument. Prior to analysis, the tin chloride solution is placed at the specified position in the instrument. Firstly, a sample is injected into the reaction vessel. Then, the lid is closed and the tin chloride solution is added to the vessel. The sample and tin chloride react in a closed system for a certain period, approximately 30 seconds, to reduce the oxidized mercury into elemental mercury. The reduced mercury is vaporized and circulates in the air of the reaction vessel. Once the reaction time has lapsed, the valve of the reaction vessel opens automatically, and mercury is introduced into the atomic absorption spectrophotometer. As the mercury in well-mixed air is introduced all at once, the signal appears as a sharp peak. The peak heights are measured and compared to obtain accurate data. After the analysis, mercury in the sample flows out of the instrument with the exhaust gas, which is trapped with an absorbing solution such as potassium permanganate.

‘27’ The operation blank is analysed first followed by the standard solutions for the calibration curve. Finally, the collected samples are analysed, including duplicates if duplicating sampling is performed. When analysing the collected samples, it is recommended that a standard sample with a moderate concentration is inserted every 10 samples to confirm that the sensitivity has not drifted. This standard solution for the calibration curve is also pre-treated by acid digestion; therefore, a sufficient quantity of the standard solution should be prepared in advance, depending on the number of samples to be analysed. If the standard solution runs out during the analysis, the operation must be interrupted. Thus, the amount of standard solution required for the entire operation should be estimated in advance.

‘28’ Once the analysis is complete, the mercury concentrations are calculated. Firstly, the calibration curve is created from the results of the standard solutions. Then, the total mercury concentrations in the samples are calculated. As the standard solutions used in this method were pre-treated by acid digestion, zero in the standard solution for the calibration curve is equivalent to the operation blank.

‘29’ The important factors for QC of the analysis are explained here. If an elevated operation blank is found after analysing the collected samples, the analysed results are not valid. Furthermore, this also results in the loss of valuable samples collected in the field. Thus, the operation blank should always be checked before analysis to confirm that satisfactory performance is possible. When an elevated operation blank is found, possible causes should be investigated, including the reagents, equipment, or other items used for the analysis operation. Once the cause is identified, appropriate measures should be taken, which may include but are not limited to improving the cleaning method for tools and obtaining reagents without a blank level.

‘30’ Duplicate analysis is performed to determine the reproducibility of the analysis, that is, to determine if the same result is obtained by analysing the same samples. It is recommended that a duplicate sample is inserted approximately once in every 10 samples. If the amount of collected sample is insufficient to conduct multiple analyses, duplicate analysis can also be performed with other samples. For example, reference materials can also be used for this purpose.

‘31’ The reproducibility of the analysis within a day can be evaluated from the duplicate analysis. It is also effective to analyse the same sample in each batch or on each day to confirm the reproducibility of the analysis on different days. Therefore, it is recommended that the results for reference materials are compared between the processed batches, usually daily. Certified reference materials, CRMs, which are commercially available, are the reference materials with traceable certified values given by national or international standards. A CRM can also be used to confirm the accuracy of the analysis results. Although CRMs are expensive for everyday use, CRM analysis at certain interval is recommended, if possible.

‘32’ Similar to the operation blank, the limit of detection, LOD, and limit of quantification, LOQ, are important factors for proper analysis and must be confirmed prior to analysing the actual samples. There are several methods for calculating the LOD and LOQ described in different manuals. Basically, these values are determined by the following two factors: the sensitivity of the instrument, which is the level that can be detected, and the degree of variation between the analysed values, which is the reliability of the obtained values. In general, the sensitivity of the instrument is evaluated based on the ratio of the signal detected for the sample and the noise of the instrument. The variability of the analysed values is evaluated using the standard deviation for repeated analysis of the operation blank and low-concentration samples. LOD and LOQ are the higher limits that fulfil these conditions.

## *Section 7: Other methods for total mercury analysis*

‘33’ A few other methods for measuring mercury in solid samples are introduced in this section.

‘34’ Thermal decomposition CVAAS is another type of mercury analysis instrument. The principle of this instrument is rather simple. Mercury is liquid at normal temperatures and vaporized at high temperatures; thus, the instrument heats the sample to decompose all mercury into a gaseous form, which is then detected by the instrument. Mercury existing as organic mercury, such as methylmercury, or oxidised mercury in the sample is mineralised or reduced during the heating process, and eventually sent to the detector in the form of elemental mercury. Although the principle is simple, the mechanism and temperature control programme are important to decompose and vaporize mercury effectively. The instrument is deliberatively designed for this purpose. The analytical operation is also simple. The sample to be analysed is placed in a vessel and loaded in the instrument together with the standard solution. Thermal decomposition CVAAS is a convenient instrumental method, as it uses very little reagent and no pre-treatment is required. However, despite the operational simplicity, the QA/QC analysis, including the operation blank, duplicates, and reference materials, is still important.

‘35’ This slide introduces an example application of thermal decomposition CVAAS. An atmospheric passive sampler made of activated carbon is used as an absorber. Collecting atmospheric mercury with a passive sampler is simply done by setting the samplers at the site for a certain period. After sampling, the sampler is analysed in the laboratory. The analysis of the activated carbon in the passive sampler can be done by acid decomposition-reduction aeration CVAAS. However, activated carbon reacts violently during acid decomposition as it is made of organic material, so special treatment and skilled operation are necessary. Therefore, thermal decomposition CVAAS is advantageous for the analysis of passive samplers. Nevertheless, a few points must be kept in mind for analysis by thermal decomposition CVAAS. Activated carbon reacts more violently than normal organic samples and may flare up in the reaction cell. To suppress this reaction, it is necessary to change the carrier gas during thermal decomposition from oxygen to air or nitrogen. If sulphur is added to the activated carbon to enhance mercury adsorption, it interferes with the mercury analysis. Thus, processes such as adding reagents that mask the released sulphur are also required. CRMs for passive samplers are not yet available, but the CRM of coal can be used as an alternative substance with similar properties.

‘36’ This slide briefly explains the screening of samples that may contain very high concentrations. Mercury-added products, waste containing mercury-added products, waste contaminated with mercury, or survey samples such as contaminated soil at gold mining sites or facilities that use mercury are very important for understanding the status of mercury pollution. However, as these samples contain intentionally added mercury or are directly contaminated with mercury, they often contain very high concentrations of mercury. For example, in the case of personal care products that use mercury as an active ingredient, the mercury content may exceed one percent, which is 10,000 ppm. If a sample containing such an extremely high concentration of mercury is unintentionally analysed in the same manner as a normal sample, it will exceed the measurable concentration range, and thus an analytical result will not be obtained. Furthermore, such high concentrations of mercury can contaminate entire laboratories, including tools and analytical instruments, which may require repair and cleaning.

‘37’ Screening to determine the mercury levels in products or waste with unknown concentrations prior to analysis will prevent improper analysis and contamination of the laboratory environment. An X-ray fluorescence analyser, XRF, is a useful instrument for screening. XRF is inferior to atomic absorption spectrophotometers in terms of measurement sensitivity, and the measurement results are affected by the material and composition of the sample. However, this instrument can measure the mercury level without pre-treatment in the laboratory. Furthermore, some XRF instruments are portable, so they are suitable for onsite screening. If a certain level of mercury is detected by XRF, the sample volume can be adjusted to fit the detection level for analysis. If the purpose of the analysis is to remediate contaminated soil, the soil can be directly removed if the mercury level in the soil detected by XRF with sufficient accuracy. If mercury is not detected by XRF, it can be assumed that the highest possible concentration is below the detection limit of XRF.

## 5.5 Lecture 4: Water sample survey and analysis

‘0’ This lecture explains the collection and analysis of water samples.

*Section 1: Key characteristics of water for mercury survey and analysis*

‘1’ The significance of mercury pollution in aquatic environments and the characteristics of water samples for survey and analysis are explained.

‘2’ This slide explains the importance of aquatic environment surveys for understanding mercury pollution. Water is an essential element for all living creatures, and aquatic environments such as oceans, rivers and lakes are very important for human life and ecosystems. Water is also an important medium for understanding the dynamics of global mercury pollution. Mercury in an aquatic environment is transported with the water stream. Ongoing chemical reactions in bodies of water, such as mercury methylation, demethylation, oxidation, and reduction are especially complex. Furthermore, mercury is often taken up from aquatic environments into the ecosystem, where bioaccumulation and biomagnification through the food chain begins. For this reason, aquatic environments are important research media from both regional and global environmental viewpoints.

‘3’ This slide describes the characteristics of water samples for mercury research and analysis. Firstly, for water samples, it should be noted that the mercury concentrations in background areas without local contamination are very low in comparison with those of other environmental media. The concentration varies due to regional and environmental factors, but a background aquatic environment survey should allow the system to be accurately analysed at a level of approximately one ng/L. For this purpose, the collected samples need to be concentrated during the analytical procedure or very sensitive analytical instruments should be used. Furthermore, the blank values from the laboratory environment, reagents, etc. become significant when analysing low concentration samples. Thus, the reduction of the operation blank level is more important than in other media. Another concern for mercury is its instability in water, which is a major difference from other metallic elements. As a result, mercury loss occurs relatively easily. Other metallic elements are not usually lost from collected water samples, but mercury may be reduced and vaporised under certain environmental conditions or penetrated through the surfaces of containers made of certain materials. Therefore, special attention must be paid to selecting the container type and to stabilizing mercury after sampling. Water samples are often larger in volume and heavier than samples in other media, partly because of the low mercury concentration. In addition, due to the instability of mercury and the risk of damage and leakage, the transportation and storage of water samples is often challenging.

*Section 2: Water sample collection*

‘4’ In this section, the procedure for collecting water samples using a water sampler is explained.

‘5’ When sampling water, a clean pail can be used, for example, for collecting drainage of water tanks in the facility or surface water in rivers, sea, etc. However, collecting water at a specific depth requires a specific water sampler. The photo shows a water sampler called a Niskin bottle, which is often used for this purpose. There are several other types of water samplers for different purposes. These water samplers are usually lowered into water with open lids, and once the target depth is reached, the lids are shut by a sinker, called a messenger, released by the operator.

‘6’ This slide explains how the Niskin bottle works. This device is actually submerged in water during operation, but the video is taken in air as the movement under water is not clearly visible. In the Niskin bottle, any part in contact with the sample water is made of resin, which is suitable for collecting water samples for surveys of metals such as mercury. As is common for many water samplers, the Niskin bottle is slowly lowered into a body of water with both the upper and lower lids open. Once the device reaches the depth for sample collection, a sinker, called a messenger, is plummeted along the wire. With the messenger hits the sampler, the lids shut and the water inside is trapped. Finally, the sampler is pulled out of the body of water to retrieve the collected water.

‘7’ This slide describes the container materials that can be used for mercury surveys. Unlike many other metals, mercury can permeate the surfaces of containers made of certain materials. Glass and fluoropolymers are suitable materials to avoid mercury permeation. Although glass is not usually a suitable material for metal surveys as it may elute the metals of interest, it can be used for mercury surveys because mercury is not contained in glass. On the contrary, containers made of polyethylene or polypropylene are not suitable as mercury permeation is relatively easy. To reduce the blank level elution from the container, it is recommended that the containers are soaked in acid solution during storage, and then cleaned with deionized water and dried on the day before sampling. It is important to mention that regardless of the container material, mercury in the water sample will be reduced and volatilised. Thus, stabilisation to prevent mercury volatilisation is always needed.

‘8’ The actual operation of water sample collection is explained here. Water samples are usually collected from a bridge or boat. The sampler is gradually lowered into the water with the top and bottom lids open. After submerging the sampler to the target depth for sampling, the messenger is plummeted along the wire. It takes some time for the messenger to hit the sampler. After waiting for the messenger to hit the sampler, the sampler is pulled up with the wire.

‘9’ Once the sampler is retrieved, the sampling cock on the sampler is opened to transfer the water into the water container. The remaining water is placed in a beaker or another receptacle to measure the water temperature and pH. Although the water temperature and pH are not necessary to analyse mercury concentration, these parameters should be measured as much as possible because they provide very important information for understanding the condition of the survey site at the time of sampling. As mercury in water samples is unstable, mercury is effectively stabilised by adding a stabilisation reagent, such as hydrochloric acid, immediately after collection. If it is not possible to do this on site, the samples should be brought back to the laboratory as soon as possible for stabilisation. Finally, the collected samples are put in plastic bags and then transported and stored under cool and dark condition.

‘10’ After sampling, the status of survey is recorded. The recording should be done at the sampling site, unless prevented by the weather or other conditions. The more time that passes after sampling, the more difficult accurate recording becomes. The information to be recorded includes the sampling date and time, operator, name and coordinates of the sampling point, sampling depth, sampler used, sampled volume, container used, water temperature, and pH. It is convenient to always use the same format for the on-site recording of the collection status for later reference. As water and sediment samplings are often carried out at the same location at the same time, developing a format that accommodates information about both water and sediment samples provide additional convenience.

‘11’ Another water sampling method using a bucket is explained here. A bucket can be used to collect near-surface water but not water in the middle or bottom layers. There are some tricks to collecting water using a rope and bucket. If the bucket is slowly lowered from a bridge or boat to the water, the bucket sits on the water surface and cannot easily scoop water. Instead, water sample can be easily collected by dropping the bucket upside down, straight onto the water. Care must be taken not to collect floating objects such as litter or oil when collecting surface water. Such objects exist only on the very surface of the water; therefore, at sample mixed with these objects may not represent the actual condition of the surface water at the sampling site. If litter or oil is identified on the surface of the water, it should be prevented from entering the bucket during water collection. As with water samplers, processes such as stabilisation and measuring the temperature and pH should also be performed.

*Section 3: Total mercury analysis for water sample*

‘12’ This section describes total mercury analysis for water samples applicable for both freshwater and sea water. The method of extracting and concentrating mercury as a dithizone complex is introduced here.

‘13’ This diagram outlines the analysis of total mercury in water samples. High-sensitivity measuring devices such as an atomic fluorescence spectrometer, AFS, are sensitive enough to measure background-level environmental water samples. When cold vapour atomic absorption spectrometer, CVAAS, is used for water samples in the general environment, mercury cannot be detected unless the sample is concentrated before analysis. Firstly, mercury in soluble and suspended forms is separated by filtration as the method only applies to dissolved mercury. Suspended matter is analysed separately as a solid. All mercury in the filtrated water sample is oxidized with potassium permanganate. Then, potassium permanganate remaining in the solution, which interferes with the process, is reduced with hydroxylamine. Mercury in the sample is extracted as a dithizone complex into a small amount of toluene. After evaporation, the complex is digested with nitric acid, perchloric acid and sulphuric acid, as is done for solid samples, and then mercury is analysed with reduction aeration CVAAS.

‘14’ The reagents used in the analysis are shown on this slide.

‘15’ As explained here, 20 normality sulphuric acid is prepared by gradually adding 60 mL of concentrated sulphuric acid into 35 mL of deionized water. Since concentrated sulphuric acid is added to a small amount of water, a significant heat of solution is generated, which may lead to boiling if prepared at room temperature. The solution is cooled in an ice water bath to avoid boiling, and sulphuric acid is added gradually to minimise the generated heat of solution.

‘16’ Sodium hydroxide does not dissolve easily when water is added all at once. It is firstly dissolved in a small amount of water to generate a heat of solution. Then, the concentration of dissolved sodium hydroxide is adjusted by adding the remaining water.

‘17’ This slide describes the preparation of a dithizone-toluene solution. Dithizone is weighed and dissolved in toluene. Then, this solution is extracted once with a 0.1 normality sodium hydroxide solution. As dithizone is a weak organic acid, it moves into the aqueous phase under alkaline conditions. After that, the solution in which dithizone is dissolved is acidified with hydrochloric acid. Under acidic conditions, dithizone becomes soluble into toluene, which enables its extraction into toluene again. Dithizone can be purified by applying this process repeatedly. As dithizone is easily decomposed, it is prepared before each analysis and kept in dark conditions when not in use.

‘18’ The analysis operation is explained here. Firstly, the water sample is placed in a separatory funnel. Then, 20 normality sulphuric acid and potassium permanganate solution are added to oxidize the mercury in the sample. The sample is left for five minutes to allow mercury to react completely.

‘19’ After five minutes, the sample is neutralised with the sodium hydroxide solution. Then, hydroxylamine is added to reduce and decompose permanganate. If the purple colour of permanganate does not disappear, more hydroxylamine should be added, as this indicates that the amount of hydroxylamine is insufficient.

‘20’ After the purple colour of permanganate disappears completely, an EDTA solution is added. Then, 10 mL of dithizone-toluene solution is precisely measured and added with a whole pipette. The sample is shaken well for one minute and then, left until toluene and water are separated.

‘21’ Once extraction with dithizone-toluene is complete, and the toluene and water phases are separated, the toluene phase is transferred from the separatory funnel into a test tube. Water still exists in the toluene phase despite the extraction process; thus, the sample is centrifuged to separate water completely. Then, exactly seven mL of the toluene solution is collected using a pipet. The solution is concentrated with a rotary evaporator to completely remove toluene, as any toluene remaining in the sample interferes with the subsequent acid digestion treatment. The concentration process should be continued until the liquid is completely gone.

‘22’ After extracting mercury with dithizone-toluene and removing the toluene completely, the sample is digested with acid by adding one mL of deionized water, two mL of a one-to-one mixture of nitric acid and perchloric acid, and five mL of sulphuric acid. The acid-added sample is digested by heating at 200 to 230 °C. If a hot plate is used, the temperature may not be sufficiently high for digestion. It is recommended that the actual temperature of the hot plate surface is measured to confirm that it is sufficient for the digestion. After digesting for 30 minutes, heating is stopped and the samples are left to cool to room temperature. Once the samples have cooled sufficiently, the volume of each sample is adjusted to 50 mL for analysis.

‘23’ In this analysis method, the standard solutions for preparing the calibration curve are extracted and digested in the same manner. When placing a sample in the separatory funnel, the same amount of deionized water is added. The numbers of the water samples prepared corresponds to the points needed for the calibration curve. Then, the standard solution is added to each separatory funnel at the amount corresponding to the concentration level of the calibration curve. An operation blank, containing only deionized water without added standard solution, is also prepared. After that, the same treatment as done for the collected samples is performed to prepare standard solutions for the calibration curve.

‘24’ Once the analytical operation has been performed, the details of the operation should be recorded immediately. The necessary information includes the pre-treatment status of the samples, that is, the date and time of treatment, the operator who performed the treatment, the amount of sample used, the amount of standard solution used, the amount of toluene used for extraction, the duration of digestion, and the final preparation volume. For later reference, it is beneficial if the record form is prepared in advance. In addition, an entry field for special notes is useful to record special situations that occur during the operation.

‘25’ Once the extraction and digestion operations are complete, both the samples and standard solutions are analysed with a reduction aeration atomic absorption spectrophotometer. A sample is placed in the reaction vessel, whose lid is closed soon after injecting the sample, and then tin chloride is added. Mercury in the sample solution in the instrument is reduced by tin chloride, vapourised and introduced into the detector. These operations differ in different types of instruments, many of which perform this process automatically. Therefore, the details should be confirmed using the instruction manual of the instrument being used. The analysis is performed in the following order: operation blank, standard solutions for the calibration curve, and collected samples. If the number of samples exceeds 10, a standard solution with a moderate concentration in the calibration curve should be analysed every 10 samples. This step is to confirm that the sensitivity of the instrument is not fluctuating. After analysing the samples, a calibration curve is created based on the data obtained for the standard solutions and the concentrations of the samples are calculated.

### *Section 4: Quality control - Reducing operation blank level*

‘26’ In this section, some means for reducing the operation blank values, which is a very important factor for quality control of the analysis of low-concentration water samples, are explained.

‘27’ Efforts should always be made so that the operation blank has the lowest value in all analyses, but this is especially important for analysing total mercury in environmental water as the mercury concentration is usually very low. If a low concentration sample such as environmental water is analysed under an analytical condition with a high operation blank, a valid value will not be obtained, and the collected sample will be lost. To avoid wasting the efforts made for sample collection and analysis, the operation blanks for the laboratory analysis must be confirmed before analysing the samples. Even if the operation blank is sufficiently low, efforts to further reduce the operation blank value should always be performed to prevent accidental increases and to improve the quality of the data. Such efforts include: reliably cleaning the sample containers and glassware used for the analysis and reagent management to prevent the use of old or potentially contaminated reagents.

‘28’ This slide explains the method for cleaning glassware. Cleaning with a potassium permanganate solution is effective for reliably removing mercury from glassware used for total mercury analysis. The glassware used or to be used for analysis is immersed in a potassium permanganate solution. If possible, it is more effective to perform ultrasonic cleaning while the glassware is immersed in the potassium permanganate solution. After cleaning with the potassium permanganate solution, the glassware is rinsed with deionized water and dried in a clean environment.

‘29’ Another method for lowering the operation blank is to treat the tin chloride used in the reducing aeration atomic absorption spectrophotometer. Commercially available tin chloride contains a trace amount of mercury, which affects the analytical results. This mercury can be removed relatively easily by blowing with nitrogen after preparing the solution. The 10 percent tin chloride solution used for the analysis is prepared by dissolving tin chloride in hydrochloric acid and then diluting with deionized water to an appropriate concentration. After that, nitrogen gas is blown into the solution to expel mercury. Blowing for approximately 30 minutes can significantly decrease blank value, but this process is more effective if done for a longer time.

## 5.6 Lecture 5: Human biological sample analysis

‘0’ This lecture explains the analysis of hair, blood, and urine, which are the media related to human health. The analysis of these media is particularly useful for the risk assessment of vulnerable populations such as children and women of child-bearing age, or high-risk groups with vocational mercury exposures.

### *Section 1: Key characteristics of human biological samples*

‘1’ Mercury is an element with many unique physicochemical properties, and its behaviour in the human body differs from that of other organic and inorganic chemical substances. This section introduces the characteristics of mercury in the human body. These unique characteristics are important factors for conducting mercury surveys in the human body.

‘2’ Hair is the most typical monitoring medium for mercury surveys. Hair can take up methylmercury during growth. The methylmercury level in hair is much higher than that in other parts of the body; therefore, hair is a very good indicator for evaluating the exposure to methylmercury. Since hair sampling is non-invasive, it does not burden the person subject to the survey very much. However, the survey should be very carefully planned, as some people or groups have cultural or customary intolerance against cutting hair. Because hair itself is a stable medium and most mercury in hair is in the form of methylmercury, samples are relatively easy to transport and store. In addition, as hair grows, the past exposure information is recorded toward the tip of the hair. Thus, analysing mercury in hair from the root to the tip can provide information about the historical methylmercury exposure of the individual.

‘3’ This slide describes the characteristics of blood samples. Blood plays an important role in the metabolism of many chemical substances in the human body, including mercury in both organic and inorganic forms. For this reason, blood can be a good indicator of both inorganic mercury and methylmercury. However, it should be noted that the level of inorganic mercury in the blood of the general population is usually low as their exposure is low. Blood sampling is an invasive means of sampling, so the risk to the person subject to blood collection is higher than the risk during hair or urine collection. Therefore, the hygienic conditions for sample collection must be properly managed. Another important aspect of mercury in blood is that most methylmercury exists in red blood cells and most inorganic mercury exists in plasma. This feature is particularly important when analysing mercury in samples other than whole blood.

‘4’ The characteristics of urine are explained in this slide. Elemental or inorganic mercury taken into the body by inhalation of mercury vapour is not accumulated in hair but mostly excreted in urine. For this reason, urine is a very good indicator for exposure to elemental or inorganic mercury. Similar to hair sampling, urine sampling is non-invasive and can be done relatively easily without much health risk to the person subject to the survey. Although sample collection is rather easy, urine samples need particular care when handling after collection. Most mercury in urine is in the form of inorganic mercury, which is unstable and easily evaporated; therefore, the collected samples should be promptly frozen or otherwise treated. If on-site stabilisation is not possible, the samples should be sent to the laboratory as soon as possible at the lowest possible temperature, and then treated using an appropriate method, such as freezing. Another important aspect, which is not limited to mercury, is that the concentration of chemical substances in urine significantly varies due to the amount of water excreted. The mercury concentration also varies in each excretion, so it is evaluated against the creatinine concentration, which is stable throughout the day. The concentrations of mercury and creatinine are analysed separately, and the body burden for the person subject to the survey is evaluated based on these concentrations.

### *Section 2: Hair sample collection*

‘5’ In this section, the procedure for collecting hair sample, which is unique to mercury surveys, is explained.

‘6’ This video shows the actual collection scene for hair samples. Firstly, approximately 20 threads of hair are grabbed and tied near the root with adhesive tape. The bundle of hair is then cut from the root with scissors so as not to injure the scalp. The collected hair is put in a container for transportation to prevent scattering and keep it away from dust. Small envelopes are suitable for this purpose. Hair sample collection itself is easy, but some care needs to be taken to avoid improper handling that will spoil the credibility of the data. It should be ensured that the hair is collected from the root so that the recent exposure status at the time of collection can be evaluated. Additionally, the hair should be securely bundled so that the bundle does not fall apart after collection. The bundle should indicate either root or tip end of the hair. It is recommended that hair is tied at the root end to confirm the direction of growth.

‘7’ After taking the collected hair back to the laboratory, the sample is cut to the required length for the purpose of the evaluation. For a person subject to methylmercury exposure, 20 threads of hair with three cm are sufficient to evaluate the exposure environment over approximately three months. After cutting the hair to the required length, it is washed with detergent to remove dust on the surface.

Then, it is rinsed well with deionized water, dried with acetone, put in a glass container such as a petri dish, and shredded into fine pieces with scissors.

### *Section 3: Total mercury analysis for human biological sample*

‘8’ The analysis of total mercury in biological samples can be performed using either acid digestion-reduced aeration atomic absorption spectrophotometer or thermal decomposition atomic absorption spectrometer. This section explains the former methodology.

‘9’ This operation flow involves the acid digestion-reduction aeration cold vapour atomic absorption spectrometry, CVAAS, analysis method. Firstly, a sample is digested with nitric acid, perchloric acid, and sulphuric acid in an open vessel. After digestion, mercury in the sample solution exists in a divalent oxidized form, which is highly soluble in water. Once mercury is reduced with tin chloride to elemental mercury, which has low water solubility, it is vaporized and introduced into the CVAAS instrument for measurement.

‘10’ Firstly, the collection of analytical samples is explained. Before measuring the actual sample, the working condition of the analytical balance is confirmed. Specifically, weights or other references are measured before using the balance every day to ensure that the correct value is displayed. Then, shredded hair is mixed thoroughly in a container, and approximately 10 mg of the sample is placed in the acid digestion vessel using tweezers or a spatula. In this video, a 50 mL volumetric flask is used for digestion, as the shape is suitable for recirculating the digestion liquid. The collected hair often adheres to the wall of the digestion vessel by static electricity. Hair adhered on the upper side of the digestion vessel is not digested sufficiently during the operation, so it should be ensured that the sample is settled at the bottom of the vessel. The use of static remover is beneficial.

‘11’ For blood and urine samples, approximately 0.5 g or two mL of sample is collected using a pipette. Attention should be paid to the formation of clots in blood or precipitates in urine, which compromise the homogeneity of the sample. The sample for analysis should be mixed well and used in a homogeneous condition.

‘12’ When collecting samples, standard solutions for calculating the sample concentrations are also prepared. Amounts of mercury corresponding to those required to create the calibration curve are taken from the standard stock solution with a syringe and placed in digestion vessels. An operation blank without any additions, that is, neither standards nor samples, is also prepared. The prepared standards are digested as done for the collected samples and analysed using CVAAS.

‘13’ To confirm the reproducibility of the analysis, that is, the difference in results for analysing the same samples, duplicate analysis should be performed at a certain frequency. Analysing the same sample twice or more is recommended approximately once in every 10 samples. The reproducibility of the analysis within a day can be evaluated by duplicate analysis. It is also effective to compare the results between different days. For this purpose, it is recommended that a reference material of the same type is analysed to confirm the variation for such reference materials on a regular basis. Certified reference materials with traceable certified values given by national or international standards are commercially available for human bio-samples. By analysing these certified reference materials in the laboratory, the accuracy of the analysis can be evaluated.

‘14’ After preparing the samples, they are digested with acid. A piece of zeolite boiling stone is placed in each sample and then one mL of deionized water, a one-to-one mixture of nitric acid and perchloric acid, and sulphuric acid are added. Then, the sample is heated and digested at approximately 200 to 230 °C. Deionized water should not be added to urine samples. After digesting for 30 minutes, the heating is stopped and the samples are left to cool to room temperature. Then, the volume of each sample is adjusted to 50mL. As soon as the digestion is conducted, the operation details should be recorded. The necessary information for this pre-treatment operation includes date and time, operator, sample amount, duration of digestion, and final preparation volume.

‘15’ After acid digestion, the sample is analysed using reduction aeration CVAAS. Firstly, the sample is placed in the reaction vessel and the lid is closed. Then, tin chloride solution is added to the vessel. Mercury in the sample solution in the instrument is reduced by tin chloride, vapourised, and introduced into the detector. These operations may differ in different instruments, many of which operate automatically, so reference should be made to the instruction manual of the instrument being used. The analysis is performed in the order of operation blank, standard solutions for the calibration curve, and then the samples to be analysed. If the number of samples exceeds 10, it is recommended that a standard solution from the middle of the calibration curve is analysed every 10 samples to confirm that the sensitivity of the instrument has not drifted. Human exposure to mercury differs substantially depending on the living environment and diet, and even a person living in a non-contaminated environment may sometimes have mercury levels beyond the range of the calibration curve. In this case, the sample should be diluted and analysed again to ensure that the concentration falls within the range of the calibration curve. After analysis of the samples, a calibration curve is prepared using the analytical results for the standard solutions to calculate the concentrations of the samples.

‘16’ This slide explains the external factors that may affect the mercury levels in hair both positively and negatively. Hair is a very good indicator for surveying people subject to methylmercury exposure.

In some cases, however, mercury may adhere to the outside of the hair. This may occur when a person is exposed to air containing high concentrations of mercury at gold mining sites or in mercury-using facilities. This may also be the case if a person is using a personal care product that contains mercury as an active ingredient. These cases may result in a high level of elemental or inorganic mercury adhered to the hair surface. Since mercury adhered to the surface is not caused by the digestion of methylmercury, it should not be assessed to evaluate the actual exposure and the risk of methylmercury. Therefore, special care must be taken when assessing hair samples with high mercury concentrations on the external surface. On the other hand, hair bleaching and permanent treatments can remove some of the methylmercury in hair. Therefore, the same care should be taken when assessing the actual methylmercury exposure. Such supplementary information can be obtained from the person subject to the survey using a questionnaire, which will provide useful information.

‘17’ The importance of infection prevention during the handling of human bio-samples is explained in this slide. Human samples such as blood may be contaminated with infectious bacteria, viruses, etc. Therefore, great care must be taken to avoid direct contact with the sample. Gloves must be used at all times when handling human specimens. The tools or devices use for analysing biological samples may cause infectious diseases if they are left unattended after use. The pipette tips and empty containers used for collecting blood samples should be disposed of as infectious waste. The glassware used for blood analysis should be soaked in a sodium hypochlorite solution for a while and then washed.

## 5.7 Lecture 6: Methylmercury analysis

‘0’ This lecture explains the analysis of methylmercury. There are several methods for analysing methylmercury. The method found in the Mercury Analysis Manual in Japan is described here.

### *Section 1: Key features of methylmercury surveys*

‘1’ This section explains the key features of methylmercury survey.

‘2’ The biological effects of methylmercury are briefly addressed in this slide. Compared to inorganic mercury, methylmercury has a longer half-life in living organisms, which makes it highly bio-accumulative. Methylmercury is known for its strong toxicity to the central nervous system. Therefore, methylmercury in the environment is accumulated in the ecosystem and exhibits high loading levels and toxicity in humans and other organisms particularly in high trophic levels. For this reason, analysing methylmercury is sometime more relevant than analysing total mercury.

‘3’ This slide highlights key features for the research and analysis of methylmercury in biota. The toxicity and bioaccumulation ability of methylmercury is significantly higher than those of other forms of mercury. The proportion of organic and inorganic mercury accumulated in the bodies of living organisms varies among species and individuals. Some species and individuals have a relatively low proportion of organic mercury in the body. Thus, assessing the methylmercury concentration in the target species is an effective means of understanding the behaviour of mercury in the ecosystem. Assessing methylmercury levels in food items is also relevant for evaluating the effect on humans accurately. The Codex Guidelines, which define food safety standards, set guideline values for methylmercury in some fish species.

‘4’ When surveying human hair, it is sometimes important to know the level of methylmercury. As hair only accumulates methylmercury in the body, all mercury in the hair should be methylmercury; however, some elemental or inorganic mercury may adhere to the hair surface if the hair is exposed to high concentrations. For example, atmospheric mercury at gold mining sites or mercury-using facilities and personal care products containing mercury are possible sources of such mercury. Mercury adhering to the surface is not accumulated by means of internal exposure to methylmercury; thus, analysing total mercury including this surface portion will provide misleading evaluation results. To assess the mercury exposure of the person subject to the survey property, methylmercury in the hair samples should be analysed if the adsorption of elemental or inorganic mercury is expected.

*Section 2: Methylmercury analysis*

‘5’ The actual analysis procedure for methylmercury is explained using fish as an example. The process employs alkaline digestion, dithizone extraction and finally analysis by gas chromatography, GC, with an electron capture detector, ECD.

‘6’ This slide shows the entire process of alkaline digestion, dithizone-toluene extraction, and GC/ECD analysis. The principle of this method is to digest the sample with an alkaline solution, and then to extract methylmercury into toluene as a dithizone complex. Organic substances other than methylmercury, which are also extracted in this method, will interfere with the analysis. The trick of this method is to remove most of the other organic substances coexisting in the sample by repeated extraction and back extraction at different pH values to refine methylmercury. The operation flow involves many steps, but this pre-treatment is normally completed in one to two days. The analysis is then performed using a GC/ECD instrument, which is cheaper than a mass spectrometer and has high sensitivity for specific substances such as methylmercury.

‘7’ The actual operations are described in videos. There are many steps in this analytical process, but similar operations are involved, which will be explained together. Firstly, a sample is weighed, and a solution of potassium hydroxide in ethanol is added. Then, the sample vessel is capped and digestion proceeds in an oil bath heated for one hour at 100 °C. As alkali decomposes proteins very well, almost no solids remain after digestion. Deliberate care should be taken in handling the alkaline ethanol solution at high temperatures, which can cause severe burns.

‘8’ After alkaline digestion of the sample, the pH is adjusted to the acidic range to extract methylmercury into the aqueous phase and separate it from coexisting lipids. Hydrochloric acid and hexane are added to the sample, which is then shaken and centrifuged to separate the hexane and aqueous phases. Then, the upper hexane phase is removed.

‘9’ After removing lipids by cleaning with hexane, the sample is extracted with a dithizone complex. An EDTA solution and a precise amount of dithizone-toluene solution are added to move methylmercury back into the toluene phase. After shaking, the sample is centrifuged to separate the phases completely, and the lower aqueous phase is removed.

‘10’ After extracting the methylmercury in the sample into toluene phase, the following steps are performed: cleaning with alkaline aqueous solution, back extracting with sodium sulphide, cleaning with toluene, acidifying and re-extracting, cleaning with alkaline aqueous solution, acidifying, and transferring to a measuring vial. These steps remove co-existing matrices by back-extracting into the aqueous phase and re-extracting into toluene. These individual operations are similar to the previous steps. Finally, the sample is prepared in a small amount of toluene and analysed by GC/ECD.

‘11’ The sample digested by alkali and refined by extraction is analysed by GC/ECD. GC/ECD instruments are cheaper than mass spectrometers and have lower maintenance costs. In this method, a packed column is used for separating large amounts of sample to lower the detection limit.

### *Section 3: Methylmercury analysis for human hair samples*

‘12’ In this section, the analysis of methylmercury in hair is explained.

‘13’ To analyse methylmercury in biological samples such as fish, a long pre-treatment involving digestion and extraction is required to remove interfering components before the sample is analysed by GC/ECD. For hair samples, methylmercury can be efficiently extracted by hydrochloric acid without digestion. Therefore, the analysis of methylmercury in hair can be conducted with a very simple operation procedure as shown in the flow.

‘14’ This slide explains the actual analytical process for analysing methylmercury in hair. Firstly, approximately 10 mg of hair is collected, and one or two drops of ethanol is added. Then, three mL of two-normality hydrochloric acid is added, and methylmercury is extracted into hydrochloric acid by heating for five minutes at 100 °C. After extraction, one mL of hydrochloric acid solution is taken from the sample, and toluene is added to transfer the methylmercury into the toluene phase. The toluene solution of extracted methylmercury is analysed by GC/ECD in the same way as other samples. Clearly, very few steps and a short time are required for hair analysis.

## 5.8 Lecture 7 Mercury monitoring and the Minamata Convention

‘0’ This lecture explains the legally-binding provisions of the Minamata Convention on Mercury particularly the Articles that are relevant to mercury monitoring in multiple media.

### *Section 1: Outlines of the Minamata Convention*

‘1’ This section explains the backgrounds and scope of the Minamata Convention on Mercury.

‘2’ The Minamata Convention on Mercury is a multilateral legally-binding environmental agreement aiming to protect the human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds. The text was adopted in October 2013 and is composed of a preambular text, 35 articles, and 5 annexes. The Convention entered into force on 16 August 2017, on the 90th day after the deposition of the 50th instrument of ratifications, acceptance, approval, or accession.

‘3’ In its preamble, the Convention recognises the substantial lessons of Minamata disease, in particular the serious health effects resulting from the mercury pollution, and makes aware of the health concerns to women, children, and future generations. The Convention sets out a range of measures throughout the entire life cycle of mercury to meet its objective. Articles 3 to 12 relate to the operational provisions describing the Parties’ obligations to reduce emissions and releases, with controls throughout their life cycle, which include measures to control the supply and trade of mercury, mercury-added products, manufacturing processes in which mercury or mercury compounds are used, as well as artisanal and small-scale gold mining, ASGM. The text also includes the articles on emissions and releases of mercury, environmentally sound interim storage, mercury waste, and contaminated sites. Articles 13 to 21 facilitate the implementation of these measures including provisions related to support for the Parties, information, awareness raising, and reporting. Articles 22 to 35 cover the overall management of the Convention. Annexes A and B list the mercury-added products and manufacturing processes to be controlled by the Convention. Annex C sets the items to be included in the national action plans for ASGM. Annex D lists the point source categories for emission control.

‘4’ The Convention covers all forms of mercury as element and mercury compounds. Specific mercury compounds are subject to control in Article 3, supply and trade, and Article 10, interim storage. Article 4 specifies mercury-added products to be phased out or phased down by the Parties.

*Section 2: Measures to reduce mercury risks*

‘5’ This section explains the measures stipulated in the Convention to reduce mercury risks to human health and the environment.

‘6’ Article 4 Mercury-added products: Each Party shall not allow the manufacture, import or export of mercury-added products listed in Part I of Annex A after the phase-out date, which is 2020 for the products originally listed. Each Party also shall take measures to phase down the use of mercury-added products listed in Part II of Annex A, which is dental amalgam. Each Party shall take measures to prevent the incorporation of mercury-added products into assembled products and discourage the manufacture and distribution of new mercury-added products. The Secretariat shall collect and maintain information on mercury-added products and make it publicly available. The Conference of the Parties, COP, shall review Annex A and may consider amendments. The first amendment was adopted by the COP at its fourth meeting in 2022, which sets the phase-out for those newly listed in 2025.

‘7’ Article 5 Manufacturing processes in which mercury or mercury compounds are used: Each Party shall not allow the use of mercury or mercury compounds in the manufacturing processes listed in Part I of Annex B, and shall take measures to restrict the use of mercury or mercury compounds in the process listed in Part II of Annex B. Each Party shall also take measures to address emissions and releases of mercury or mercury compounds from these facilities. Each Party shall not allow the use of mercury or mercury compounds in new facilities and shall discourage their use of mercury or mercury compounds in new processes. The Secretariat shall collect and maintain information on processes using mercury or mercury compounds and make it publicly available. The COP shall review Annex B and may consider amendments.

‘8’ Article 7 Artisanal and small-scale gold mining: Each Party with ASGM in its territory shall take steps to reduce, and where feasible eliminate, the use, emissions and releases of mercury and its compounds. Each Party with more than insignificant ASGM in its territory shall notify the Secretariat and develop and implement a national action plan, which shall be submitted to the Secretariat within three years after the development of the plan. Thereafter, a review of the progress made shall be conducted every 3 years.

‘9’ Article 8 Emissions: A Party with relevant sources shall take measures to control emissions from sources listed in Annex D. Each Party shall require the use of best available techniques, BAT, and best environmental practices, BEP, to control emissions for new sources within five years after becoming a Party and implement one or more measures for existing sources within 10 years after becoming a Party. Each Party shall also establish and maintain an inventory of emissions. The COP adopted the guidance on BAT/BEP, including goals and emission limit values for existing sources, the guidance on criteria to identify source categories, and methodology for preparing inventory. The BAT/BEP guidance was adopted by the COP at its first meeting in 2017.

‘10’ Article 9 Releases: Each Party shall identify the relevant point source categories, which are not addressed in the other provision of the Convention, no later than three years and on a regular basis thereafter. Each Party shall take measures to control releases, and establish and maintain an inventory of releases. The COP shall adopt guidance on BAT/BEP and methodology for preparing inventories.

‘11’ Article 11 Mercury wastes: Mercury wastes means substances or object consisting of, containing or contaminated with mercury or mercury compounds in a quantity above the relevant thresholds defined by the COP. Each Party shall take measures to manage mercury waste in an environmentally sound manner. Each Party shall also ensure that the recovery, recycling, reclamation or direct re-use of mercury waste is for an allowed purpose or for environmentally sound disposal only. For the Party to the Basel Convention, mercury waste shall not be transported across international boundaries except for the purpose of environmentally sound disposal. The COP shall define relevant thresholds for mercury wastes.

‘12’ Article 12 Contaminated sites: Each Party shall endeavour to develop appropriate strategies for identifying and assessing sites contaminated by mercury or mercury compounds. Actions to reduce the risks shall be performed in an environmentally sound manner. The COP adopted guidance on managing contaminated sites in its third meeting in 2019.

### *Section 3: Provisions facilitating the implementation of measures*

‘13’ This section explains the provisions of the Conventions that facilitate the Parties implementing the measures to fulfil the objective of the Convention.

‘14’ Article 16 Health aspects: Parties are encouraged to promote the development and implementation of strategies and programmes to identify and protect populations at risk. They are also encouraged to promote the development and implementation of science-based educational and preventive programmes on occupational exposure to mercury and mercury compounds, and to promote appropriate health-care services for prevention, treatment, and care for populations affected by the exposure to mercury or mercury compounds. Furthermore, they are encouraged to establish and strengthen the institutional and health professional capacities for the prevention, diagnosis, treatment, and monitoring of health risks related to the exposure to mercury and mercury compounds.

‘15’ Article 18 Public information, awareness, and education: Each Party shall promote and facilitate the provision to the public of available information, and education, training and public awareness related to the effects of exposure to mercury and mercury compounds.

‘16’ Article 19 Research, development and monitoring: Parties shall endeavour to cooperate to develop and improve inventories of use, consumption, and anthropogenic emissions and releases of mercury. The cooperation also includes modelling and monitoring of mercury in vulnerable populations and in environmental media, assessments of the impact of mercury on human health and the environment, in addition to social, economic, and cultural impacts, information on the environmental cycle, transport, transformation and fate of mercury, information on commerce and trade in mercury and mercury-added products, and information and research on the technical and economic availability of mercury-free products and processes and on BAT/BEP to reduce and monitor emissions and releases of mercury. Additionally, Parties should build on existing monitoring networks and research programmes.

### *Section 4: Overall management of the Convention*

‘17’ This section explains the provisions of the Conventions that provide overall management of the Convention particularly evaluating the effectiveness of measures to achieve the objective of the Convention.

‘18’ Article 22 Effectiveness evaluation: The COP shall evaluate the effectiveness of the Convention, beginning no later than six years after entry into force and periodically thereafter. To facilitate the evaluation, the COP shall initiate the establishment of arrangements for providing itself with comparable monitoring data on the presence and movement of mercury in the environment, and trends in levels of mercury observed in biotic media and vulnerable populations.

‘19’ The evaluation shall be conducted on the basis of available scientific, environmental, technical, financial and economic information including reports and other monitoring information, national reports submitted, information and recommendations on compliance provided, and reports and other relevant information on the operation of the financial assistance, technology transfer and capacity-building arrangements.

### *Section 5: Contribution of mercury monitoring to the Convention*

‘20’ This section describes the value of mercury monitoring for the effective implementation of the Minamata Convention.

‘21’ The Minamata Convention explicitly and implicitly refers to the monitoring required for its effective implementation. Mercury monitoring facilitates the implementation of some measures. The levels of mercury in environmental media or in products indicate the mercury risks to be reduced. Geographical and temporal profiles of mercury levels are key data for evaluating the overall effectiveness of the Convention.

‘22’ The mercury contents of products such as batteries, lamps, cosmetics, and pesticides can be used for import and export control as well as domestic market surveys. Skin whitening cosmetics are still widely used by many women in the societies where lighter coloured skin is preferred. The same information can also be used to estimate mercury stock in society and to forecast mercury waste generation. Emissions and releases can be monitored to assess the environmental impacts of mercury source facilities. Contamination surveys of environmental media can provide important data for public information and awareness. Mercury monitoring is also essential for the sound management of mercury waste.

‘23’ The human health concerns of mercury are twofold, namely health and safety in the workplace and environmental health for vulnerable population such as pregnant women. As methylmercury, inorganic mercury, and elemental mercury exhibit different toxicities in humans, mercury speciation is important for proper risk assessments. From a scientific perspective, mercury monitoring is essential for research activities that provide improved knowledge about the fate and transport of mercury as well as mathematical models for forecasting future trends. Additionally, the presence and movement of mercury in the atmosphere as well as trends in biotic media and vulnerable populations, such as children and women of child-bearing age, are useful for evaluating the effectiveness of the Convention.

## 5.9 Lecture 8: Quality management

‘0’ This lecture explains the quality management of analytical data by referring to the definitions provided by the International Organization for Standardization, ISO.

*Section 1: Outlines of TQM, QA, and QC.*

‘1’ This section outlines total quality management, TQM, quality assurance, QA, and quality control, QC. QA and QC are often confused. These explanations also include some terminology.

‘2’ This slide shows the general principle of TQM. In fact, there is no clear definition of TQM provided by ISO, or others. The general principle can typically be understood as an "all embracing discipline to ensure the organization’s output".

‘3’ This slide shows the seven principles of quality management defined in ISO 9000. They are customer focus, leadership, engagement of people, process approach, improvement, evidence-based decision making, and relationship management. These principles are described in ISO 9000, but this idea applies universally across the management systems issued by ISO, including ISO/IEC 17025, where the system requirements are defined using the same philosophy.

‘4’ ‘Quality improvement’ is included in the configuration of TQM. It has often been questioned why quality must be continuously improved, as quality beyond the current criteria would be excessive. This criticism is refuted by the following explanation. Among industrial products with the same performance specifications, products of good quality are sold at a high price. Analytical data is not a commercial commodity per se, but high-quality data could create great value. For example, highly accurate data can provide qualified information to the subject with fewer samples. Thus, improving quality may offer new knowledge that was not previously understood.

‘5’ This slide explains the important points of a quality management system for an organization. These are not the exact terms defined by ISO or others, but could be summarised by the seven principles in the requirements of the ISO 9000 series and ISO/IEC 17025. They are clarified policy and objectives of the system, documented protocol for the purpose, clear framework of the system, properly obtained evidence, and appropriate resource management of human, material, budget, time, and information necessary for system operation. In a quality management system, it is important that these elements are clearly documented, properly implemented, and securely recorded.

‘6’ This slide indicates the necessary check items for quality management. Are the policy and objective clear? Is the procedure appropriate? Are the rules and procedures fully documented? Are the resources managed appropriately? Is the process conducted correctly? Is there sufficient evidence? Is the quality of the products adequate? Are there sufficient check procedures and evidence? It is necessary to check these items and correct them, if they are insufficient, throughout the system design and implementation. The first four are particularly important in system design, and the last two are important in system operation.

‘7’ It is important to keep in mind that quality management has its own purpose, which is not for the sake of obtaining ISO accreditation. The quality management process can be cumbersome as it requires more steps. However, the quality management process clarifies the quality of laboratory data, that is, accuracy, and makes it comparable with other data. Maintaining and continuously improving the quality of data is the real value of quality management. It is emphasized that high-quality data creates new value, such as discovering new knowledge; thus, the improvement in data quality can be considered an improvement in the capacity of the laboratory.

### *Section 2: SOP and record: Process clarity*

‘8’ This section explains the items relevant to QC. There are two important components for process clarity: a standard operating procedure, SOP, and a record.

‘9’ ISO defines the term QA as the "part of quality management focused on providing confidence that quality requirements will be fulfilled". QC is defined as the "part of quality management focused on fulfilling quality requirements". Both QA and QC are considered part of overall quality management.

‘10’Firstly, the meaning of the ‘quality’ in terms of analysis should be clarified. Since the obtained data is the product of analytical activity, the quality of the analysis can be referred to as the quality of data itself. How should the quality of data be measured? The quality of analytical data means the degree of accuracy. Therefore, error in analytical data is the most important quality management component. In general, errors are divided into bias from the true value and the uncertainty of the result. The quality management of analysis is an activity to evaluate the magnitude of these errors and to reduce such errors continuously.

‘11’ This slide explains how the quality of analytical data can be ensured. The quality of analytical data should be ensured from two aspects: the adequacy of the process employed and the result obtained. The adequacy of the process is ensured by a set of documents, including a clearly refined SOP, evidence of correct operation that records that the operation was performed correctly according to the SOP, and evidence of schedule control that ensures that the activities in the analysis were appropriately done. The adequacy of the result is also ensured by a combination of several types of information, including the results of QC test samples such as operation blanks, duplicate analysis, standards reference materials, evaluations of the experimentally obtained limit of detection, limit of quantification, and uncertainty, and the results of proficiency tests conducted between laboratories.

‘12’ This slide explains the roles and effects of an SOP, which is an important document for determining the analytical process. The key role of the SOP in quality management is to clarify the process of operation to avoid different operations being performed on different occasions or by different operators. The documented SOP enables people outside of the system to objectively confirm the operations being performed. The SOP in written form is an effective means of preventing changes that may affect the results during the analytical operation, which tends to drift gradually over time or with the replacement of operators. Other benefits of having an SOP include the easy education and training of operation staff, and easy technology transfer to other laboratories.

‘13’ The key considerations for preparing an SOP are explained in this slide. Firstly, different from manuals, SOPs are developed from the viewpoint of facilitating the actual operations in a laboratory. The descriptions of the operations should be simple enough to be understood easily when performing the operations. Additionally, the operational tips and warnings should be put on the same page or close to it for easy reference instead of summarised on a separate page. On the other hand, while keeping the descriptions as simple as possible, the SOP should include all factors that affect the analytical data, such as the amount of sample to be used, the amounts of reagents, and the reaction temperature and duration. Without clear instructions on these elements, the quality of data may vary on different operation dates or with different operators; therefore, these elements should be addressed in the SOP. If some of the operation parameters in an SOP have been changed due to improvements of the analysis method, such changes should be reflected in the SOP and the effective date should be indicated.

‘14’ This slide shows a few more tips for developing an SOP. To make it simple and easy to understand, it is recommended that figures and photos are used effectively. When the contents of the SOP are revised, the effective date will be very important when later checking the data. Thus, whenever the SOP is revised, the effective date should be indicated, and the old version should be removed promptly to prevent misuse. SOPs for sample management, such as sample naming, ID assignment, classification, transportation, and storage, should be developed in addition to the analytical operations to clarify the process of sample management. This is very important as failures due to improper sample management frequently occur. Sometimes, preparatory tests may have been carried out to determine some parameters, such as the amounts of reagents used in the SOP. Attaching these test data to the SOP will be very useful when verifying analysis results or improving the operations.

‘15’ The record is another important factor for ensuring the analysis process. An SOP is developed to clarify the operation of the analysis, but the actual analysis must be performed accordingly. A record is essential evidence to prove that the analytical operations were performed according to the SOP. Detailed records are not only very useful for proof of operation but also for proper data collection. Analytical data may sometimes exhibit anomalies with values outside the normal data range or different trends from past data series. In such cases, the detailed record from the time of analysis will help to determine whether the cause of the anomaly was an analytical error or a valid reason due to the situation of the survey location or sample. In addition, the accumulation of past analysis records can provide a reference of similar examples when analysing a special sample or a reference for considering appropriate countermeasures based on the analysis situation of normal samples.

‘16’ This slide explains the key considerations when deciding the contents of the record. In actual analytical operations, many items, such as the amount of reagent to be added and, the heating time., rarely change and do not seem to differ in each analytical operation. Although it may seem meaningless to record these items for each operation, it is actually useful to ensure correct operations; thus, such information should be recorded each time, to the extent possible. It is Important to note that the record is not the end product but is the information to be referred to at a later time. Therefore, a record form should be prepared for easier reference in the future. It is also important to assign a unique ID to each analytical samples and enter it in the record to identify the samples referred to in the record. The date and time of analysis, the operator, and the laboratory room, if there are more than one, are some easily forgotten but important information for quality management. The record form should be prepared to accommodate this information. During the analytical operations, some abnormal situations may occur. A remark column in the record form can accommodate such observations, which will benefit future analysis.

### *Section 3: QA/QC analysis of samples: Result validity*

‘17’ In this section, the use of operation blanks, duplicate analysis, and standard samples for evaluating the validity of analytical data are explained.

‘18’ The operation blank has great impact on the accuracy of analysis and the detection limit, so its level must be minimised. Mostly, the operation blank level in chemical analysis comes from contamination of the air in the laboratory, elution from materials or residues of previous samples on the glassware, accidental spillage of the target substances from other samples or standard solutions during operation, or contamination of the initial reagents. For mercury analysis, the air in the laboratory usually does not affect the blank, except in the case of ultra-trace analysis of samples such as ocean water. Therefore, other factors, such as contamination of the apparatus or reagents and contamination from other samples, need to be considered. The glassware must be thoroughly cleaned after use so that no mercury from the sample remains. Soaking in acid, even in dilute solutions, is an effective means of cleaning. Additionally, droplets of a sample solution are often inadvertently dropped into other samples, blanks, or standard solutions. The analytical operation should be carefully performed to avoid the mixing of such droplets, known as cross-contamination.

‘19’ Cross-contamination from the sample container or apparatus used for analysis can be avoided by thorough careful cleaning. On the other hand, the effect of trace mercury in reagents is not easy to eliminate. The best and simplest solution is to switch the reagent for mercury-free one. If this is not possible, the analysis must be undertaken with a certain blank level. It is assumed that the amounts of reagents used for an analysis are usually the same for all samples and standard solutions; thus, all the samples and standard solutions might be affected by the reagent to more or less the same degree. If the deviation of the operation blank is estimated in advance and proven to be sufficiently smaller than the actual sample concentration, the effect of the blank can be eliminated by subtracting the value from the analysed concentrations of the samples and standard solutions. The deviation of the operation blank is also related to the detection limit, which affects the accuracy of analysis and the detection limit to a great extent. It may not be possible to obtain data that meets the purpose of the survey if the blank value is larger than expected. It is particularly important to estimate the level and deviation of the operation blank prior to the actual analysis to ensure that the analytical operation meets the purpose of the survey.

‘20’ Duplicate analysis involves multiple analyses of the same samples. It is performed to check the reproducibility of the analysis. The same samples are analysed more than twice with the same procedure and the differences are compared. To understand the general situation in the analysis, the sample to be duplicated for analysis should be selected from among the samples with typical properties. Additionally, a sample with a concentration that is sufficiently higher than the detection limit should be selected to verify the differences among the analytical results. In some cases, the amount of sample is not sufficient for multiple analyses. Duplicate analysis may also be performed with another sample with similar properties prepared for that purpose and analysed together with the analytical samples.

‘21’ The reproducibility of the analysis within the same day can be assessed using the duplicate analysis information, but the most effective way to confirm the reproducibility of the analysis between different days is to analyse the same samples on every day of analysis. For this reason, it is recommended that the same sample is analysed and the results are compared for each processing batch for analysis, usually daily. Certified reference materials, CRMs, which have been evaluated jointly by many analytical institutions and given a certified value, are commercially available for use in the laboratory as a standard material. CRMs can be used to assess the reproducibility of the analysis. Since the certified value is traceable to the national or international standard, CRM analysis is a very useful method for understanding the level of bias in the analytical data of the laboratory. CRMs are expensive materials for use in daily analysis, but it is recommended that such as analysis is performed on a regular basis, if possible.

‘22’ As the name implies, CRMs are standard materials with certified values. The certified value is usually obtained through joint experiments by multiple analytical institutions, so that the traceability of the analysis is guaranteed and the uncertainty is estimated. The number after the plus-minus sign in the certified value is sometimes misunderstood. The numerical value described as zero-point yy is the uncertainty of the given certified value, that is, the degree of accuracy of the certified value. It should be noted that this number is not the value obtained by the actual analysis of the CRM. Instead, the uncertainty of CRM is estimated from multiple analysis data, and not all analysis results fall within this range. Therefore, using this range to control the CRM analysis may disqualify laboratory results that were actually completed properly. It should be noted that the criteria of the CRM analysis should consider both the uncertainty of the certified value and the uncertainty of the analysis conducted in the laboratory.

‘23’ The use of limit of detection, LOD, and limit of quantification, LOQ for QA/QC is explained here. If the LOD of the analysis exceeds the concentrations of most of the samples, the survey may not fulfil its purpose as these samples will be classified as “not detected”. To ensure that sufficient analytical data is obtained to fulfil the purpose of the survey, the lowest value that is detectable in the laboratory should be estimated prior to the analysis. The LOD and LOQ may change when the analysis situation is changed due to the replacement or repair of analytical instruments, or other reasons. In such cases, the values should be re-evaluated.

‘24’ The LOD and LOQ of the analysis need to be estimated from two perspectives. One is the limit at which the measurement signal of the sample can be certainly detected, which is a judgment based on the sensitivity of the instrument. The other is the reliability of the data obtained in the analysis, which is a judgment based on the quantification of the results. For the sensitivity of the instrument, the fluctuation of the baseline without a sample signal is considered noise; thus, the signal of mercury must be sufficiently larger than the noise to detect the mercury in the sample. In many cases, the signal is considered detectable when it is at least three times larger than the noise. The results are considered quantifiable when the variation in the analytical results for a sample is sufficiently smaller than the analytical value of the sample. This is determined by repeated analysis of the operation blank or the sample with the lowest possible concentration, ideally close to the expected LOD. The analytical value that are sufficiently larger than these deviations are estimated as the LOD and LOQ. Several methods have been proposed in various manuals and surveys to calculate the LOD and LOQ from repeated analyses. One example proposes that the LOD is estimated as three times the standard deviation and the LOQ as 10 times the standard deviation for repeated analyses. Another method calculates these values from the t value of the analysis results.

‘25’ A frequently asked question is, "How should the criteria be determined?". It is not possible to determine absolute criteria for QA/QC sample data without considering the objective or circumstances of the survey or analysis. The acceptable quality of data differs depending on the objective of the survey or analysis. The QA/QC sample criteria must consider the objective of the analysis normally performed in the laboratory. For example, the criteria for the operation blank should be determined with the required LOD, and the criteria for duplicate analysis must consider the acceptable uncertainty. The reference material criteria should also take into account the acceptable bias and the uncertainty of the laboratory analysis. The QA/QC criteria described in manuals are determined based on the quality expected when the analysis operation is performed properly.

### *Section 4: Quality of data: Bias and uncertainty*

‘26’ The most important factors for data quality are their errors, biases and uncertainties. This section outlines two of these factors: bias and uncertainty.

‘27’ Firstly, the text of Article 22 of the Minamata Convention on Mercury is shown here. The article mentions the establishment of arrangements for providing itself with comparable monitoring data on the presence and movement of mercury and mercury compounds in the environment as well as trends in levels of mercury and mercury compounds observed in biotic media and vulnerable populations. It refers to comparable data, but what does comparable data mean?

‘28’ By its nature, data is always compared with something. For example, it can be compared in chronological order with past or future data, compared with points that are spatially, geographically, hydraulically, or meteorologically relevant, or compared with administrative standards or health risks. In this sense, the data is retrieved for comparison. In many cases, the data is compared with data obtained by many other institutions. This is especially significant when the purpose of the data acquisition includes global environmental studies, such as the effectiveness evaluation of the Minamata Convention. Therefore, data comparability is a very important concept.

‘29’ The importance of data comparability was emphasized but not defined in the Minamata Convention. The important factors for data comparability are objectivity, reproducibility, and robustness. The following items are relevant for ensuring the comparability of data: the procedure is obvious, the method has been verified, an external audit verification has been performed, and the uncertainty and bias have been verified.

‘30’ This slide illustrates data bias and uncertainty schematically. The centre of the circular target in this figure indicates the true value, and the + marks indicate the obtained analysis data. The target on the left has a small bias but a large uncertainty, that is, good accuracy but bad precision. The + marks are scattered around the centre of the target. On the other hand, the target on the right has a large bias but a small uncertainty, that is, good precision but bad accuracy. The + marks are concentrated in a small area away from the centre of the target. As efforts should be made to improve both accuracy and precision in the analysis, properly evaluating the bias and uncertainty of the obtained data is a very important factor for understanding and comparing the data.

‘31’ The accuracy and precision can also be described statistically. The blue line in the figure indicates the relationship between the data value and frequency. Bias is the difference between the analysed average value and the true value, that is, the accuracy. As the true value cannot be obtained analytically, an accurate bias value cannot be determined for the analytical data. If the analytical data is obtained using a traceable system calibrated with national or international standards, the bias of the data can be evaluated against these standards, and the data can be precisely compared with other data evaluated in the same manner. Uncertainty is the degree of data variability when a sample is analysed, that is, the precision. The uncertainty of an analysis can be estimated experimentally and analytically. The comparison of analysed data with other data becomes possible through the evaluation of the bias and uncertainty of the analysis.

### *Section 5: Bias of data*

‘32’ This section describes traceability as a means of assessing data bias against standards.

‘33’ The term traceability is defined as the "property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty". Therefore, the fact that traceability is guaranteed means that the bias of data from the national or international standards is accurately estimated. For data secured by traceability in alignment with a standard, the bias against each other can be evaluated through the standard, even if the true value of the analysis cannot be known.

‘34’ A comparative test between laboratories or a proficiency test is also effective for evaluating the bias between laboratories. This test simply organizes multiple laboratories to analyse the same parameter in the same sample and compares the results. Participating laboratories can see the differences from other laboratories or standard laboratories, from which they can obtain information about data bias between their own and other laboratories.

### *Section 6: Uncertainty*

‘35’ Another important factor, uncertainty, is explained in this section.

‘36’ The term uncertainty is defined as "non-negative parameters characterizing the dispersion of the quantity values being attributed to a measurand based on the information used". Uncertainty is a value obtained by testing and calculation, which is referred to as "based on the information used".

‘37’ The process for estimating the uncertainty is explained here. Firstly, the analytical operations are examined to extract possible factors affecting the data uncertainty for evaluation. A schematic figure called a cause-and-effect diagram or fishbone chart is used for quality management. In this case, the diagram contains possible uncertainty factors involved in total mercury analysis with acid digestion. The fishbone chart relates elements that are possible factors that may affect the uncertainty and puts them in their respective places. This chart helps in developing logical discussions. It cannot directly estimate the uncertainty but serves as an effective tool to identify relevant points for quality management including the uncertainty, and to discuss improvement measures.

‘38’ Once the factors affecting the uncertainty of analysis are identified, the contribution of each factor to the uncertainty is estimated. In the “Guide to the expression of uncertainty in measurement”, GUM in short, two approaches for the evaluation of uncertainty are described. Type A is a method deriving uncertainty from actual measured values statistically, and type B is a method deriving uncertainty by other means than type A.

‘39’ The uncertainty assessment using the Type A approach is described here. The idea of Type A is rather simple. The standard deviation is calculated from actual measurements conducted multiple times. For example, the uncertainty in the amount of standard solution added is evaluated by actually collecting the standard solution multiple times with a pipette or syringe and measuring the mass to calculate the standard deviation. The uncertainty of operation by Type A is the standard deviation obtained from the measurements. It is not commonly practised in analytical operations but if the average value of multiple operations is used, the uncertainty is the standard deviation divided by the square root of the number of measurements.

‘40’ Type B applies to all information obtained by methods other than Type A. For example, a calibration report for an analytical instrument, the manufacturer’s specifications, the guaranteed value of the product, reference data taken from handbooks, or data from manuals and textbooks.

Some of these data sources, such as calibration reports, describe the uncertainty itself, but in many cases, the uncertainty is not directly reported. In such cases, the uncertainty needs to be evaluated, for example, by assuming a probability distribution for the data.

‘41’ The uncertainty evaluated from the guaranteed value is used as an example of the Type B approach. When assessing the volume uncertainty of a pipette or volumetric flask, which have guaranteed volume values, uncertainty cannot be calculated because it is unclear how the actual values are distributed. In this case, the uncertainty can be estimated by assuming a probability distribution. If the data is assumed to be distributed to the normal distribution, the approximate uncertainty can be obtained from a triangular distribution, as shown on the right side of the slide. If the data is assumed to be distributed uniformly within the guaranteed value range, the uncertainty can be calculated by assuming a rectangular distribution.

‘42’ Once the uncertainty of each element contributing to the uncertainty of the analysis is estimated, they are combined to obtain an overall uncertainty. As shown in the formula, the squared values of individual uncertainty elements are used due to the propagation law of uncertainty and then summed to estimate the overall uncertainty. There are many elements affecting uncertainty in analytical operations as was shown in the fishbone chart. The magnitude of each element needs to be considered, but it is not necessary to estimate and calculate the values for all of them. As shown in the formula, the individual uncertainty elements are squared, thus there is little contribution from the individual uncertainty elements that are less than one tenth of the maximum value. For this reason, the elements that are sufficiently smaller than the maximum value do not need to be included in the calculation. The uncertainty is calculated this way, but in many cases, the extended uncertainty is obtained by multiplying the uncertainty by a factor to increase the range of probabilities that the uncertainty covers. As shown at the bottom of the slide, the expanded uncertainty is calculated by multiplying the uncertainty by a coverage factor, to which a value of two is usually assigned. The uncertainty is based on the standard deviation, so double the standard deviation covers approximately 95% of the probability distribution.

‘43’ A frequently asked question is, “How much uncertainty is sufficient?” This depends on the objective of the survey or experiment. Analyses are performed with various objectives, such as verifying the compliance of standard values, monitoring spatial or temporal trends, or evaluating the significance of differences between target groups. When evaluating the groups with small difference, uncertainty of the analysis must be reduced. On the other hand, a relatively higher uncertainty of analysis might be sufficient if there are larger differences between the subjects to be evaluated.

‘44’ High-quality data has greater value and one of the factors affecting quality is uncertainty. When judging the difference between target populations as being statistically significant, an analysis operation with higher uncertainty may not be able to conclude that there is a difference, even though the subjects might have verifiable differences. Additionally, when analytical data is used for parameters such as in environmental models, the uncertainty of analysis directly affects the precision of the model.

‘45’ This slide provides an example of data uncertainty affecting the judgment of data reading. Both the red and yellow plots are dispersed with the same variability around the lines. Although both gradually decrease to the right, the trend in the red plot is obscured due to the uncertainty of the data. The trend in the yellow plot is obvious despite the data uncertainty because the decreasing trend is large enough.

‘46’ This slide provides an image of the significant differences between different case scenarios. As shown in the figure on the left, a significant difference can be determined if the difference between the targets is sufficiently large, even though the variation of the cases is large. If the difference between the cases becomes smaller while the variation remains large, as is shown in the centre, it may not be possible to conclude that the difference has significance. On the contrary, even if the difference between the targets is small, it may be judged that the difference is significant if the variation becomes sufficiently smaller. In real cases, the uncertainty of analysis does not always affect significant differences, as target populations also have internal variation. Nevertheless, uncertainty must be managed appropriately as it may affect the interpretation of the data.

# 5.10 Lecture 9: Laboratory safety and environmental management

‘0’ This lecture explains safety and environmental management in the laboratory, which is not directly related to survey analysis. These items are basic but important for workers’ safety and reducing environmental impacts., so they should be well understood.

### *Section 1: Safe laboratory operation*

‘1’ This section describes basic precautions when handling hazardous reagents such as acids.

‘2’ Protective goggles should be worn if reagents may be scattered by heat digestion or other operations. When transferring samples or reagents, a safety pipette filler should always be used instead of sucking with the mouth. Operations generating hazardous fumes, such as acid digestion, should be performed in a fume hood.

‘3’ Despite having safety measures put in place, accidents sometimes happen. If an acid or other hazardous reagent adheres to the skin, it should be washed off immediately with plenty of water. Even when wearing protective goggles, droplets of a reagent could possibly get into the eyes through the gaps. An eye washing bottle is effective for washing reagents out of the eyes.

### *Section 2: Safe handling of hazardous reagents*

‘4’ This section identifies reagents that are highly hazardous and require safe handling, especially those that are often used in mercury analysis. These reagents have their own unique properties. Understanding their properties is very important in laboratory safety management.

‘5’ Hydrochloric acid is a strong acid and vapour at room temperature. An aqueous solution of hydrochloric acid is used as a reagent, which is prepared by dissolving hydrogen chloride in water. Hydrochloric acid itself is a vapour, and due to this property, it gradually evaporates from its concentrated solution. Therefore, a safety mask should be worn to avoid inhaling the vapour when handling this acid. Hydrochloric acid is classified as a strong acid, but it is weaker than sulphuric acid. The mixing of hydrochloric acid with sulphuric acid results in the release of hydrochloric acid vapour into the atmosphere. Therefore, hydrochloric acid should never be mixed with a sulphuric acid solution. Hydrochloric acid is reduced in the presence of strong oxidants, and reduced chlorine ions form chlorine gas; thus, mixing hydrochloric acid with an oxidant is extremely dangerous. For example, potassium permanganate, a strong oxidant used for mercury analysis, should never be mixed with a solution containing hydrochloric acid

‘6’ Sulphuric acid is explained in this slide. Many people believe that sulphuric acid is very dangerous; however, this fear often arises from a poor understanding of its properties, which leads to it not being handled correctly. Understanding the properties of sulphuric acid and handling it as shown on this slide will lead to safe laboratory operation. Sulphuric acid is, of course, a very strong acid and corrodes many metals. It is a non-volatile acid, meaning that it is not volatilized into the atmosphere, unlike hydrochloric acid. Therefore, if dilute sulphuric acid solution adheres to skin or clothes, it becomes more concentrated as water evaporates, which causes skin burns. Sulphuric acid also has a very strong dehydration capacity. Concentrated sulphuric acid shows a strong digestive ability for many organic substances, as it affects hydrogen and oxygen in organic substances. A few other important properties include a high heat of solution in water and the strong oxidizing capacity of hot concentrated sulphuric acid. Another important note for handling sulphuric acid is that it often causes almost no pain to the skin in contract to hydrochloric acid or nitric acid. Thus, laboratory workers can experience skin burns without having noticed that sulphuric acid was adhered to their skin or clothes. If there is any possibility of contact with sulphuric acid, the affected part should be washed with plenty of water. One should also be mindful to keep paper, cloth, metal, etc. away when handling sulphuric acid. As sulphuric acid has a high heat of solution, explosive boiling may occur when adding water for dilution. When diluting sulphuric acid, it should be added into water little by little. If it is necessary to dissolve sulphuric acid in a small amount of water, for example, to prepare 20 normality solution, the process should be conducted under cooling conditions with ice water to limit the increase in temperature.

‘7’ Nitric acid is explained in this slide. Different from hydrochloric acid and sulphuric acid, nitric acid is both a strong acid and an oxidant, with the oxidizing potential being maintained regardless of its concentration. Due to this property, nitric acid corrodes many metals. When heated, it produces nitric acid vapour and nitrogen oxide gas as a decomposition product, both of which are toxic to humans. Additionally, it may be noted that nitrogen is a nutrient for plants and may lead the blooming of phytoplankton, although this is not relevant to the laboratory safety. Nitric acid should be handled cautiously to avoid inhalation of and dermal contact with the toxic vapour generated during heating operations. In addition, as nitric acid has an oxidizing capacity, it is dangerous, particularly in the event of fire. Thus, nitric acid should be stored away from strongly reactive substances, particularly metals, combustibles, and reducing agents.

‘8’ Perchloric acid is explained in this slide. Perchloric acid is a strong acid and has a very strong oxidizing potential, which makes it highly reactive and explosive on some occasions. However, perchloric acid in aqueous solution is relatively stable and often used in acid decomposition. This is very useful for sample digestion due to the high reactivity of perchloric acid. Nevertheless, there is a risk of explosion if handled incorrectly; thus, correct handling procedures should be put in place. When conducting heat digestion with perchloric acid, nitric acid should always be used together with perchloric acid. Additionally, the treated samples should never be dried, as perchloric acid becomes unstable without water and can easily explode. Perchloric acid also generates a hazardous gas containing hydrochloric acid during digestion operations. It should be handled cautiously to avoid inhalation of and dermal contact with its toxic vapour.

‘9’ This slide explains the special precautions required for basic or alkaline solutions such as sodium hydroxide. The hazardous properties of basic solutions seem to be less recognized than those of acids. In fact, strong alkalis are very hazardous to humans. They have a strong ability to digest proteins, which results in severe burns and can especially cause serious damage to the eyes. Alcohol solutions of alkalis are more permeable to the skin, which risks more serious burns. Basic reagents such as sodium hydroxide have high heats of solution in water, which may cause a fine alkaline mist to be emitted into the air when preparing an aqueous solution. As explained, strong alkaline solutions are very harmful, similar to acids and other harmful reagents. Thus, the same level of protective measures should be taken, such as wearing gloves and protective goggles when handling alkaline solutions. Mists of strong alkalis generated during operations should not be inhaled.

‘10’ The handling of organic solvents is explained in this slide. The analysis of mercury does not very often require the use of organic solvents but small amounts of organic solvent, such as toluene, hexane, and ethanol, may be used for some analyses. These three solvents are volatile with relatively low boiling points, which may cause an inhalation risk during handling. The flash points are also low, and these solvents may ignite at room temperature. Needless to say, when handling organic solvents, gloves and other protective gear should be used to minimize exposure. In addition, sufficient ventilation should be provided in the handling area and operations should be performed in a location free from fire.

### *Section 3: Apparatus and equipment safety*

‘11’ In this section, safety management for handling glassware and equipment is explained.

‘12’ Glassware is the most common cause of injury in chemical laboratories. Glassware in its proper shape will not cause injures very often. Injuries are caused by fragments of broken or chipped glassware. Broken glass is sharp and can sometimes pierce deeply. If the glassware breaks during a forced operation, it can pierce even deeper into the skin.

‘13’ As glassware is used in laboratory, the edge is occasionally chipped. There are many injuries caused by the edge of glassware. Such glassware should not be used or the chipped edge should be repaired using a burner. Many injuries are also caused by picking up pieces of glassware that was accidentally broken. A broom or other tools should be used for collection, or if picking by hand, thick gloves should be used. As the appearance of glassware does not when heated, burns caused by hot glassware or injuries caused by dropping hot glassware are also common. Deliberate care should be taken when handling apparatus that may still be hot after heat digestion.

‘14’ Sometimes, the lid sticks to glassware and cannot be removed. In such a case, forcibly removing the lid may result in breakage and injury; therefore, the lid should not be twisted by force or with tools. It is also not recommended that glassware is heated to remove the lid, as this may damage the glassware and cause serious injury. Boiling water or fire should never be used to remove the lid of glassware. If the lid cannot be removed, the area around the lid should be repeatedly tapped to unscrew it gradually and patiently. It is also effective to use an ultrasonic bath.

‘15’ Fire is the most important concern when using electric appliances. Reagents such as acids used in the laboratory can damage the electric wires, plugs, and outlets of electrical appliances, which may cause a fire due to high temperatures or electric sparks. When using electric appliances, the condition of the wires, plugs, and outlets should be examined, and damaged parts should be repaired or replaced. It is safer to connect the plug of an electric appliance only when the apparatus is in use and to disconnect it after use. If power outlets are located near the floor, the plugs or outlets of electrical appliances may get wet. When using outlets located near the floor, water use in the laboratory should be carefully controlled.

### *Section 4: Environmental management*

‘16’ In this section, environmental management in the laboratory including wastewater and exhaust gas management are explained.

‘17’ Even when a laboratory is working on environmental issues, it also impacts the environment during operation. For example, laboratory activities constantly consume resources such as reagents, electricity, water, and paper. Laboratory activities also result in the generation of wastewater, exhaust gases, and solid waste. Although it may not be possible to eliminate these issues completely, efforts to reduce the environmental impact must continue.

‘18’ Wastewater that is hazardous to the environment must be collected and treated properly and must not be released directly into the environment. Besides wastewater containing hazardous substances such as heavy metals, strongly acidic or alkaline wastewater must also be collected, regardless of whether it contains hazardous substances. In some cases, acidic or alkaline wastewater may be neutralized to remove its harm and then released if no other hazardous substances remain in the wastewater. Usually, most laboratories outsource the treatment of collected wastewater. When outsourcing treatment, wastewater should be collected and kept separately based on the type of substances it contains. To facilitate subsequent treatment, the different types should not be mixed altogether. The type of wastewater and the contained substances should be indicated on the container for safety and proper management during storage.

‘19’ Analytical operations that generate harmful gases, such as acid digestion, should be performed in a fume hood. The air discharged from the hood contains acid gas or vapour, which must be removed before release into the atmosphere to avoid environmental impact. Since the exhaust cannot be collected and stored, the acid in the exhaust from the fume hood should be removed by a gas scrubber. There are several types of gas scrubbers that can be installed indoors or outdoors. The choice of a suitable scrubber depends on the laboratory situation. If a large amount of organic solvents is used in a fume hood, which is not often the case with mercury analysis, the generated organic gas is not removed by standard gas scrubbers. When a fume hood is used for this purpose, an activated carbon filter or other device that removes organic gas is required.

## *Section 5: ISO 14001 environmental management standard*

‘20’ A standard for environmental management systems, ISO14000, is briefly introduced in this section.

‘21’ The ISO 14000 series, including ISO 14001, is a standard for developing environmental management systems. The difference from other quality standards such as ISO 9001 or ISO/IEC 17025 is that the ISO 14000 series covers all the activities of an organization to manage the environmental impact of the organization instead of focusing on specific activities. The environmental impact of each activity of the organization are extracted and evaluated. A documented environment management system based on the evaluated information is created. The system is implemented, the outcome is confirmed, and the system and activities are continuously improved. This flow is the same as the PDCA cycle in quality management systems. This means that the environmental management system is similar to the quality management system.

‘22’ The benefits of introducing the ISO 14001 system have been explained in many places, including by ISO itself. The benefits particular to the analytical laboratory are discussed and explained here. Firstly, the environmental impact of the laboratory is systematically clarified and evaluated. Laboratory activities are complex and use many chemicals, so some environmental impact might be forgotten or neglected. Systematic environmental impact assessments help reduce such oversights. Thus, the planning of environmental impact assessments facilitates easier management. The operational advantage of the environmental management system in ISO 14000 is its similarity to the quality management system. As it belongs to the same family of ISO standards, it is understandable to the analytical staff of the laboratory and relatively easy to introduce and implement. Although it is not always necessary to obtain ISO 14001 certification, this series is nevertheless a very useful system regardless of having certification. Assessing the environmental impact in alignment with ISO 14000 and managing the laboratory accordingly will reduce the environmental impact. Therefore, it is recommended that analytical laboratories incorporate this system into their management.

# 6 LIST OF ANNEXES

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| Annex C | Lecture 3: Solid sample (soil, sediment, and biota) survey and analysis (PowerPoint) |
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| Annex I | Lecture 9: Laboratory safety and environmental management (PowerPoint) |

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UNEP (2022). *Training package for mercury monitoring to enhance national capacity to generate internationally comparable scientific data*, Users' manual, version 1.0. Bangkok: UNEP.

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