Atmospheric Survey and Analysis (Manual Active Sampling Method)

UN environment programme

Sample Collection

Outlines of Atmospheric Mercury Survey

Type of Atmospheric Mercury Survey

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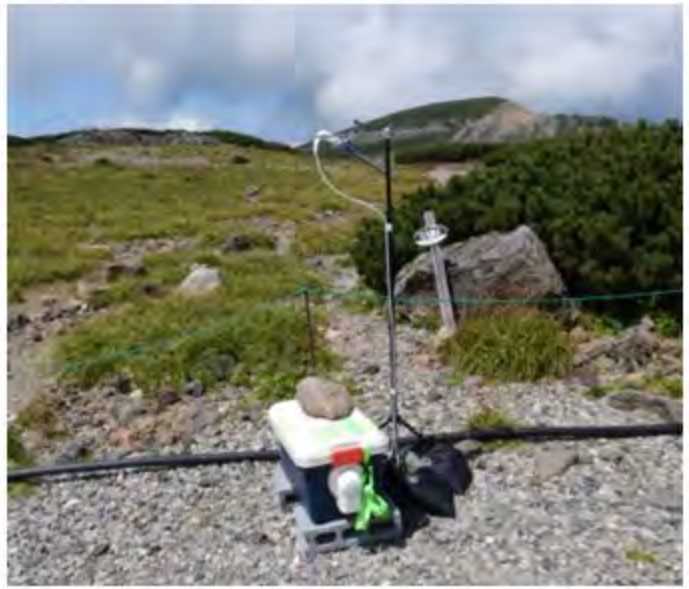
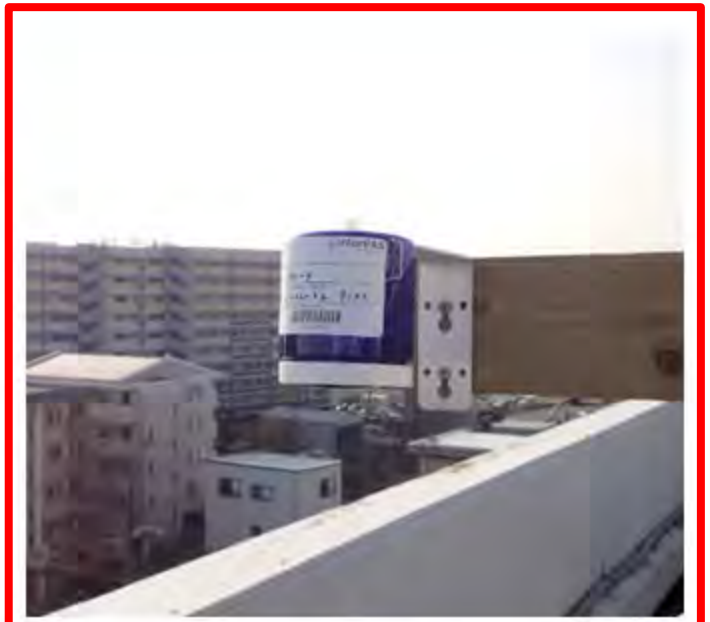
Categorized by the method of sample (air) collection

Automated active sampling

Manual active sampling

Passive sampling





Outline of Manual Active Sampling Method (Gold Amalgamation Trap)

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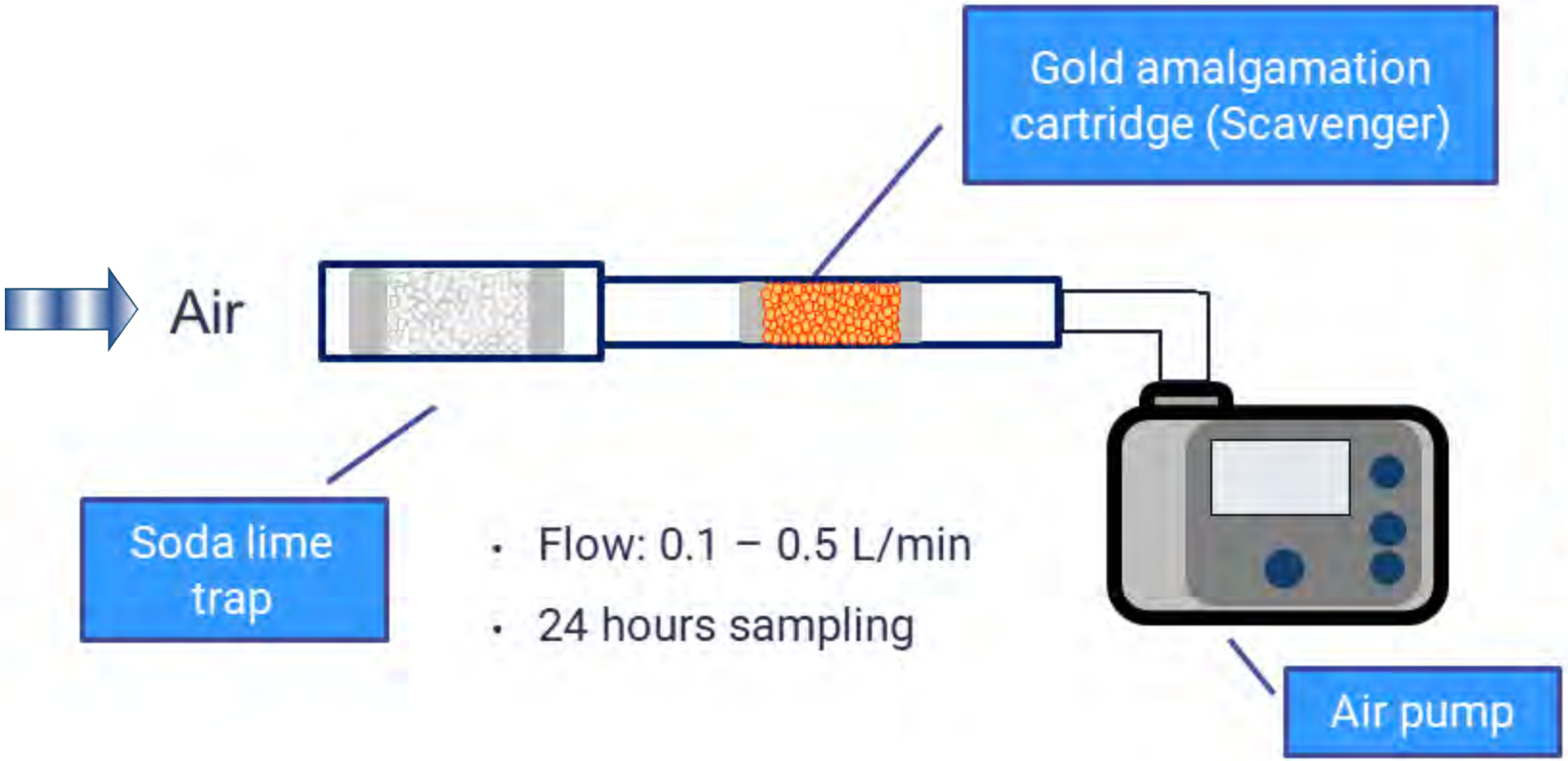
Gold Amalgamation Trap Method

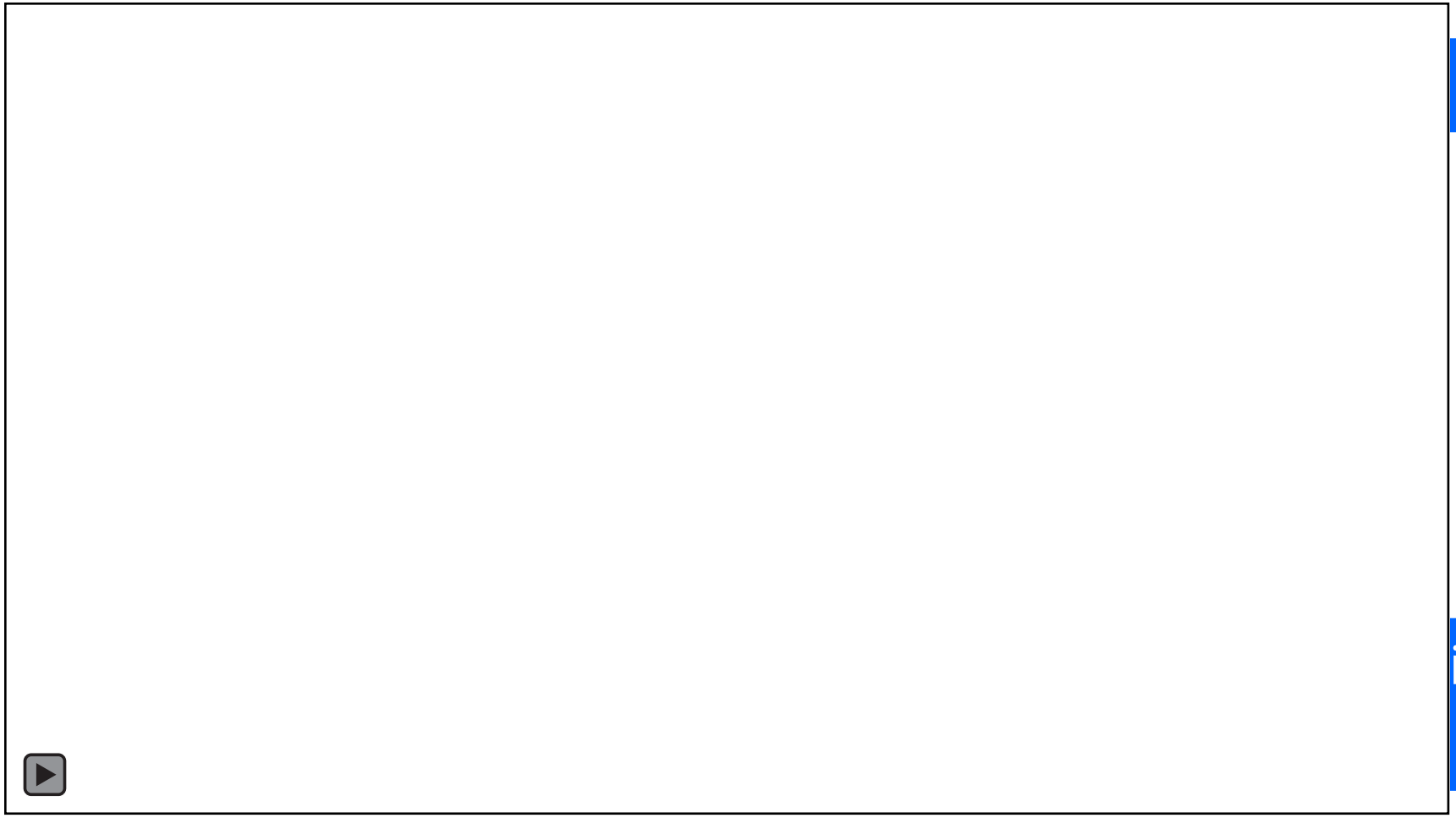


- Flow: 0.1 – 0.5 L/min
- 24 hours sampling

- ❑ Collected cartridge is easy to carry and store
- ❑ Reusable

Sampling Equipment and its Preparation

Sampling Equipment



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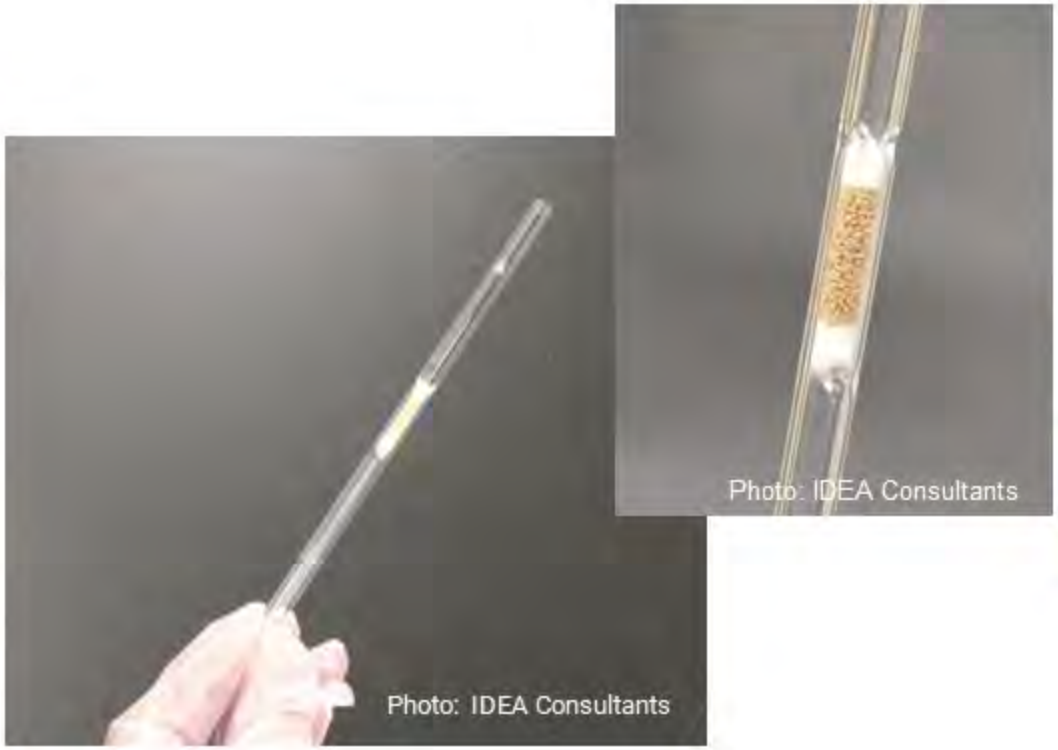
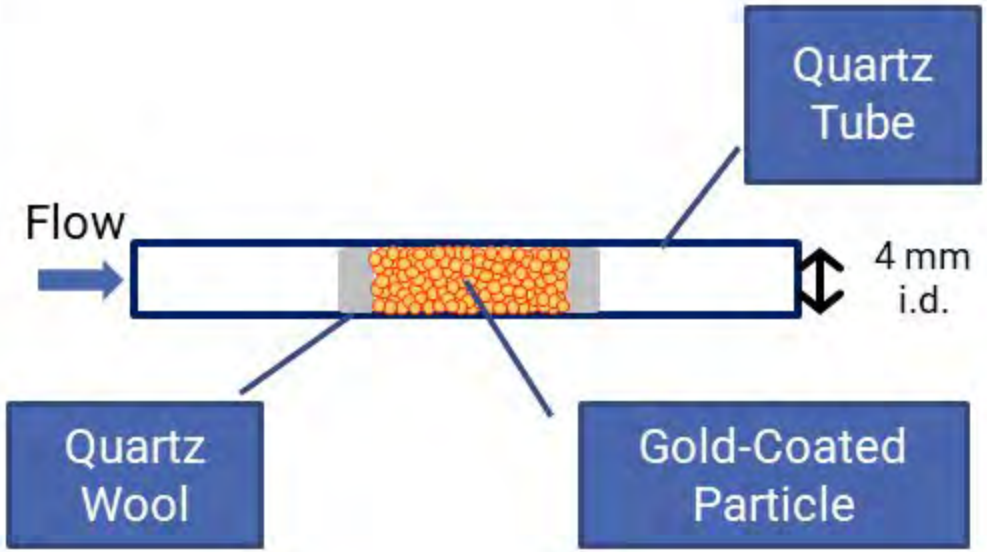
Gold Amalgamation Trap





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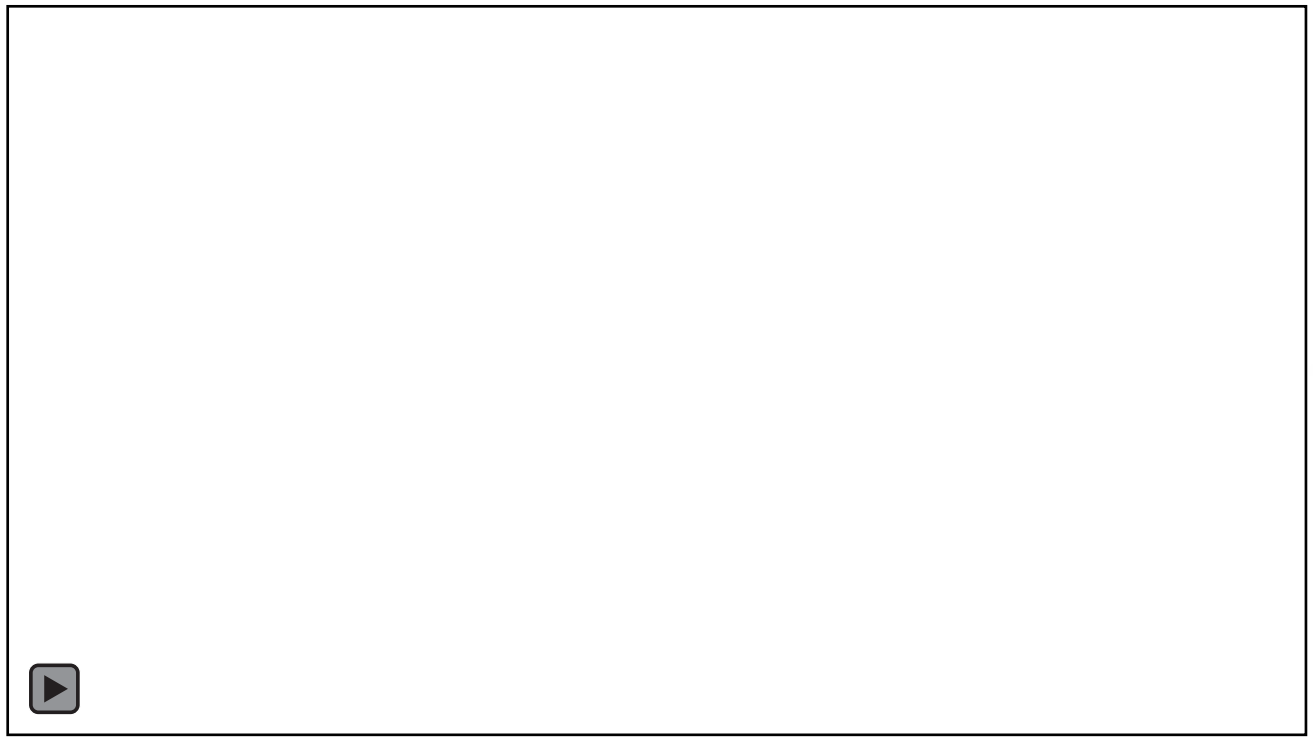
Atmospheric Survey and Analysis (Manual Active Sampling Method)

Sample Collection

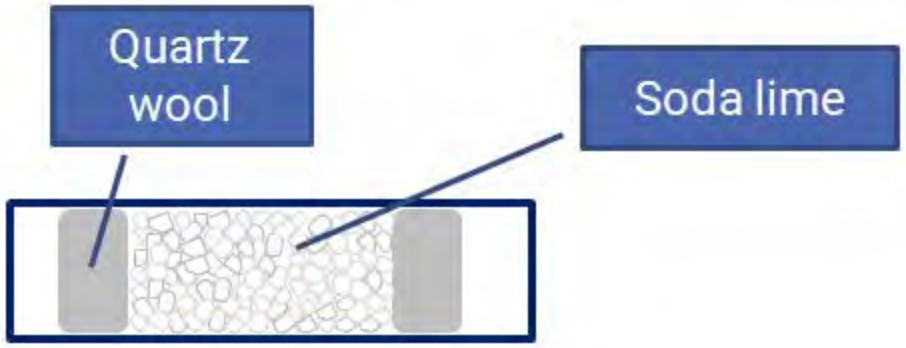
Sampling Equipment and its Preparation

Gold Trap Cartridge Preparation



- ❑Clean the cartridge by heating. (It is convenient to measure by instrument.)
- ❑Cleaned cartridge should be stored in sealed container.
- ❑Periodical “Field Blank” test should be operated.

Soda lime Trap



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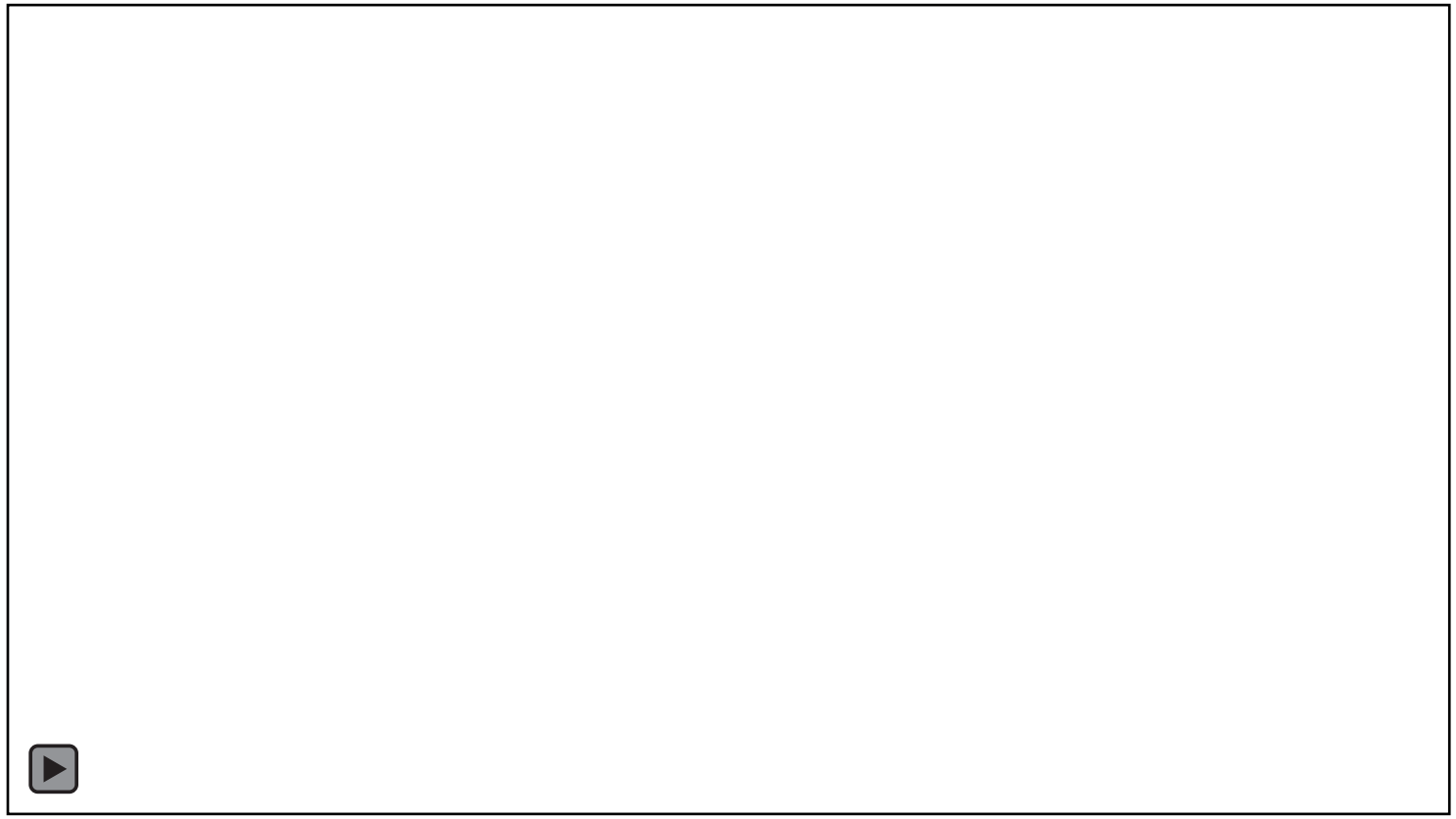
Soda lime Trap Preparation



New soda lime should be used for each sample collection

Air Pump

- Flow: ~ 0.5L / min
- Flow integrator is also necessary.
  (There are pumps which combine flow controller / integrator.)
- To convert the concentration into standard condition, Information of temperature and air pressure is also needed.

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Tubes

- Silicon rubber or other sort of plastic.
- No need to be made of glass/fluoropolymer.
- On sample collection, it should be confirmed that tubes are clean and no leakage.

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Thermometer, Barometer etc.

- Weather information is important (necessary) to assess the sampling situation.
- If there are weather monitoring station near the sampling site, that data can be used.

Atmospheric Sample Collection

Sampling Location

- ❑No mercury emission facility near the site
- ❑No special (local) air flow pattern

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Preparation of sampling point

- If the ground is bare soil, or with a lot of dust, covering with a sheet is desirable.
- A shelter to protect the pump from rain and direct sunlight, is necessary (a small tent is sufficient. Or a container with a fan for heat removal may be used.)

Stand and Pipe for Gold Cartridge

- Gold cartridge should be set at 1.5m or more from the ground.
- Pipe to protect cartridge from the rain, dust, etc.

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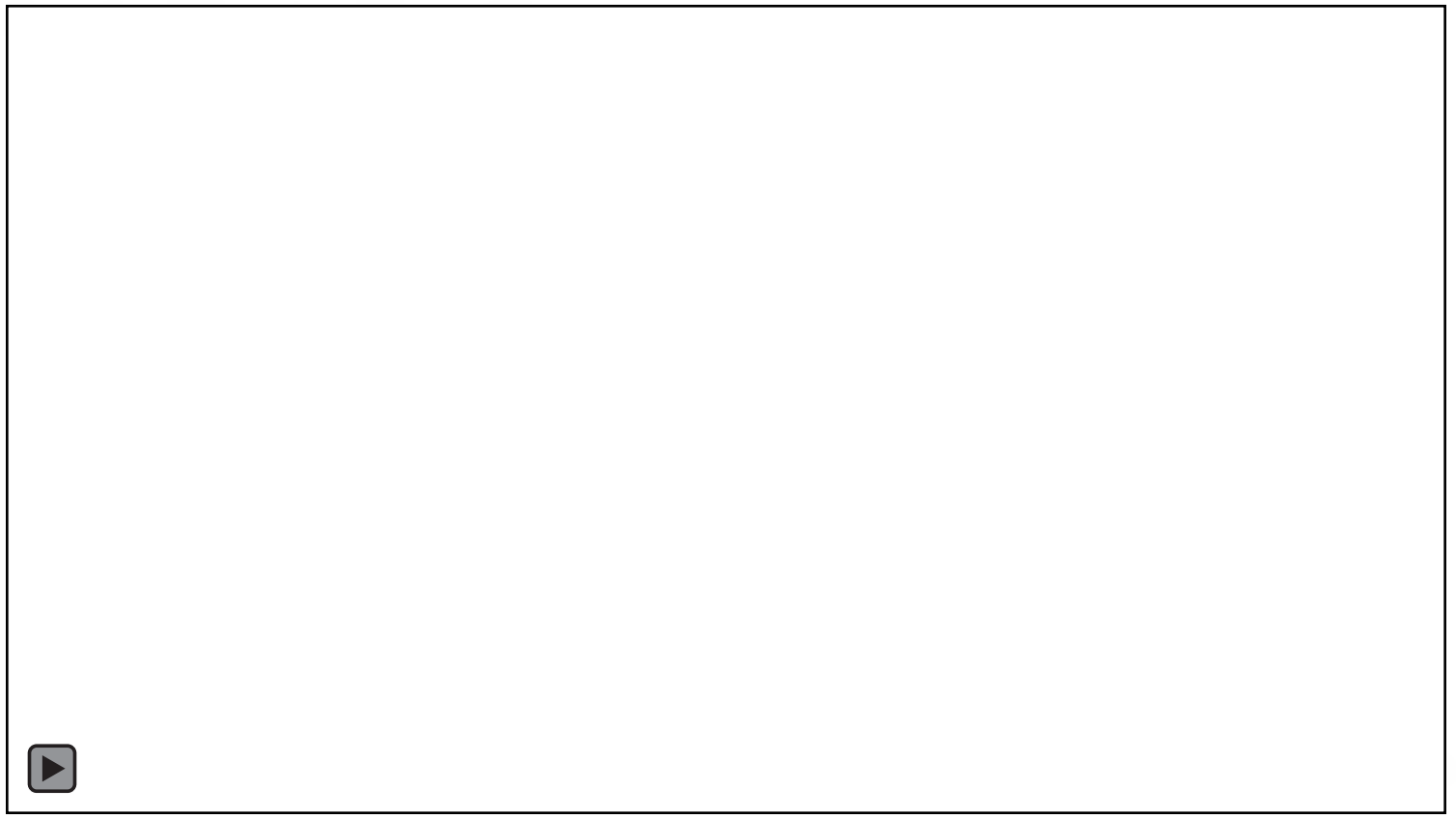
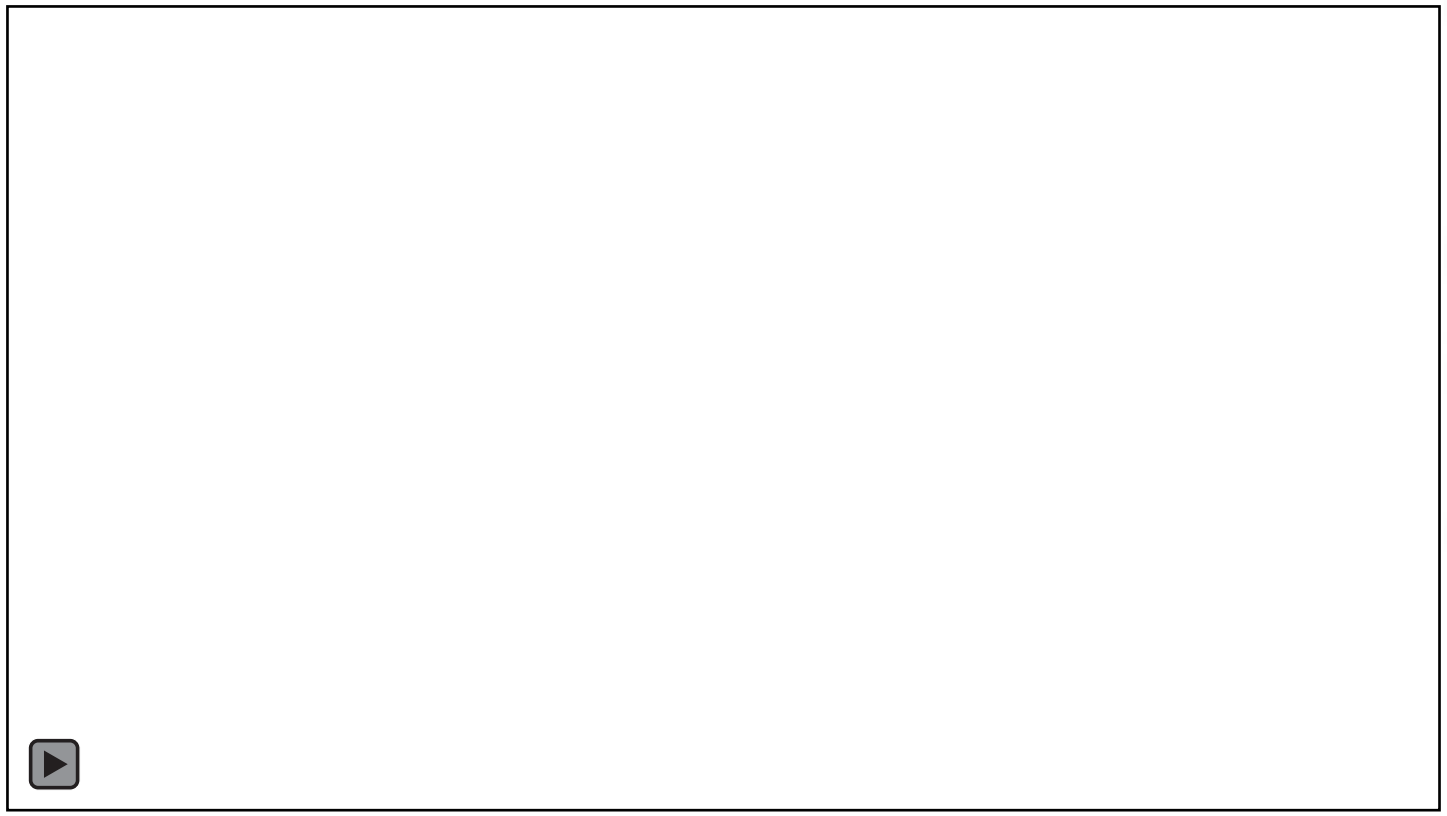
Tubing, Connection of Pump

- Check operation of the pump

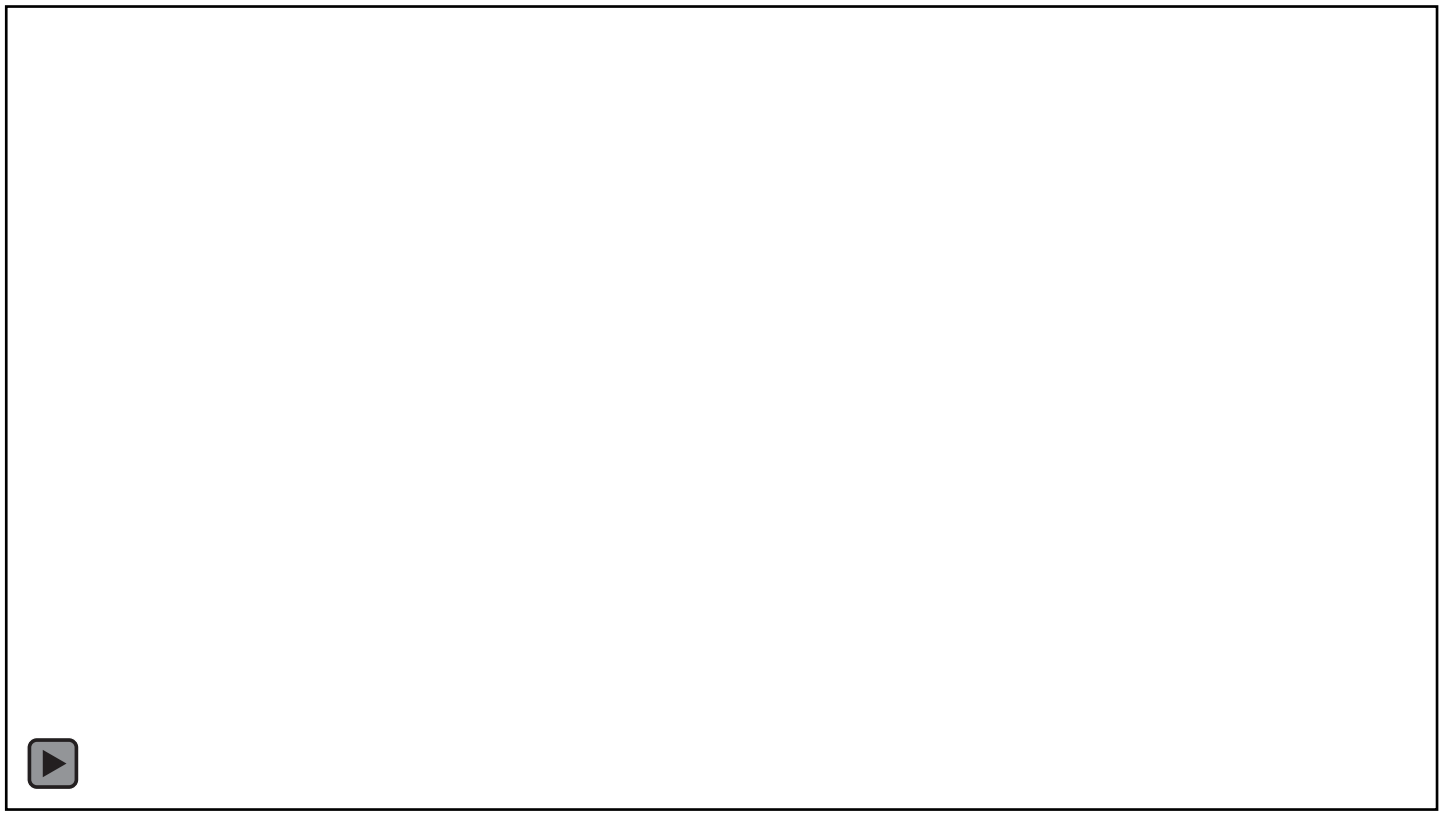


Setting-up Gold Cartridge



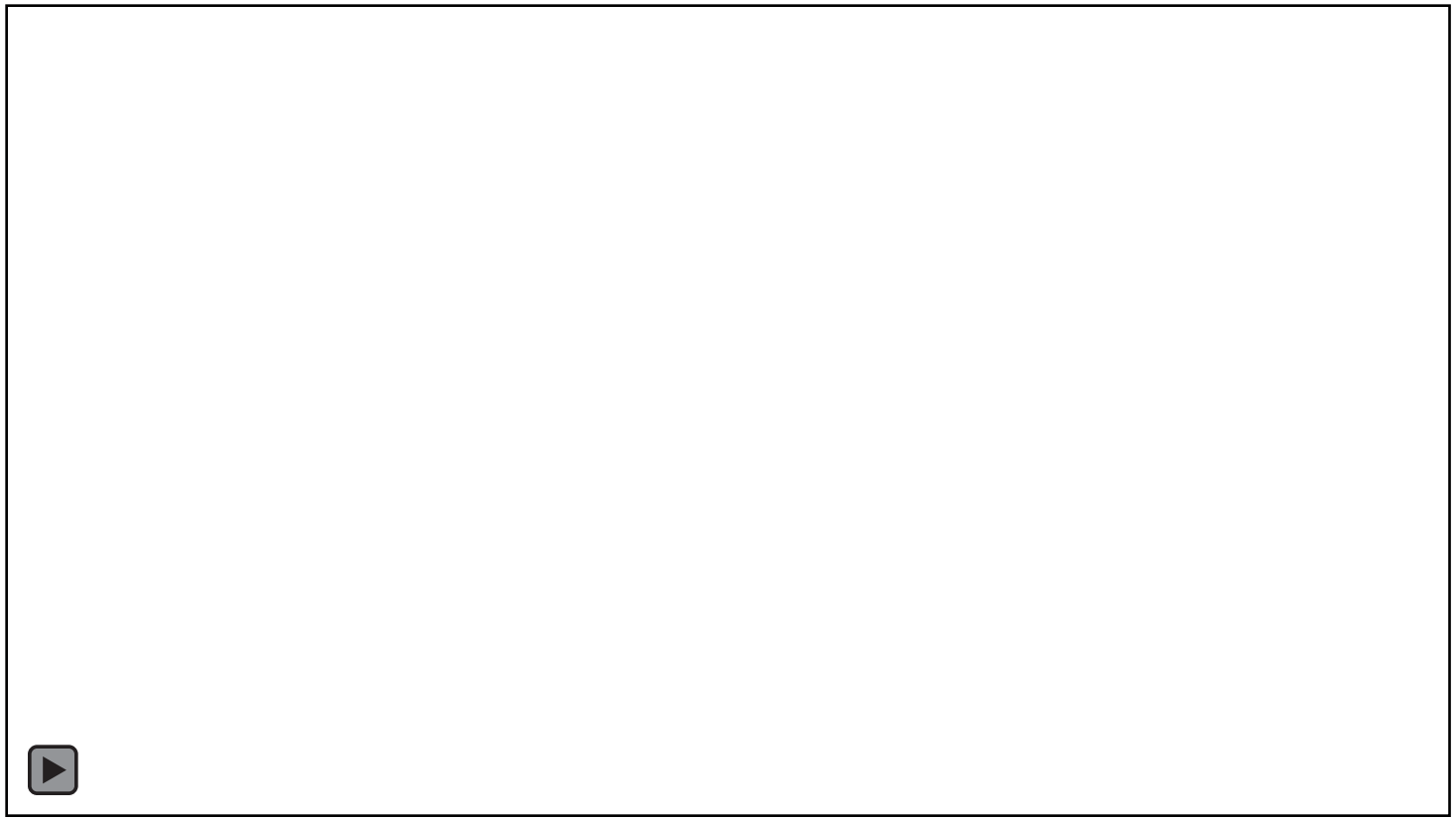
- ❑ Wear groves
- ❑ Open the Field blank case
- ❑ Take the sample cartridge, check the direction, connect the soda lime trap
- ❑ Connect the cartridge and the tube
- ❑ Tilt the sampling pipe
- ❑ Cover the end of pipe with aluminum foil

Check Connection



- ❑ Correct cartridge direction?
- ❑ No damage on the tube?
- ❑ No air leak?

Start sampling



- ❑ Start the pump
- ❑ Check the flow condition
- ❑ After starting the pump, close the container of field blanks

Recording

- Write the note at the sampling point

Photo: IDEA Consultants

Field Note

Researcher	Keisuke Uchida								
Location	IDEA Consultants, Inc. Institute of Environmental Ecology St. 1								
Condition of Sampling start up	M/D/Y	10 / 11 / 2021	Weather	Cloudy	Air temp. (℃)	18.5	Atmosphere (hpa)	1014.9	
Condition of sampling end	M/D/Y	10 / 12 / 2021	Weather	Sunny	Air temp. (℃)	21.2	Atmosphere (hpa)	1012.5	

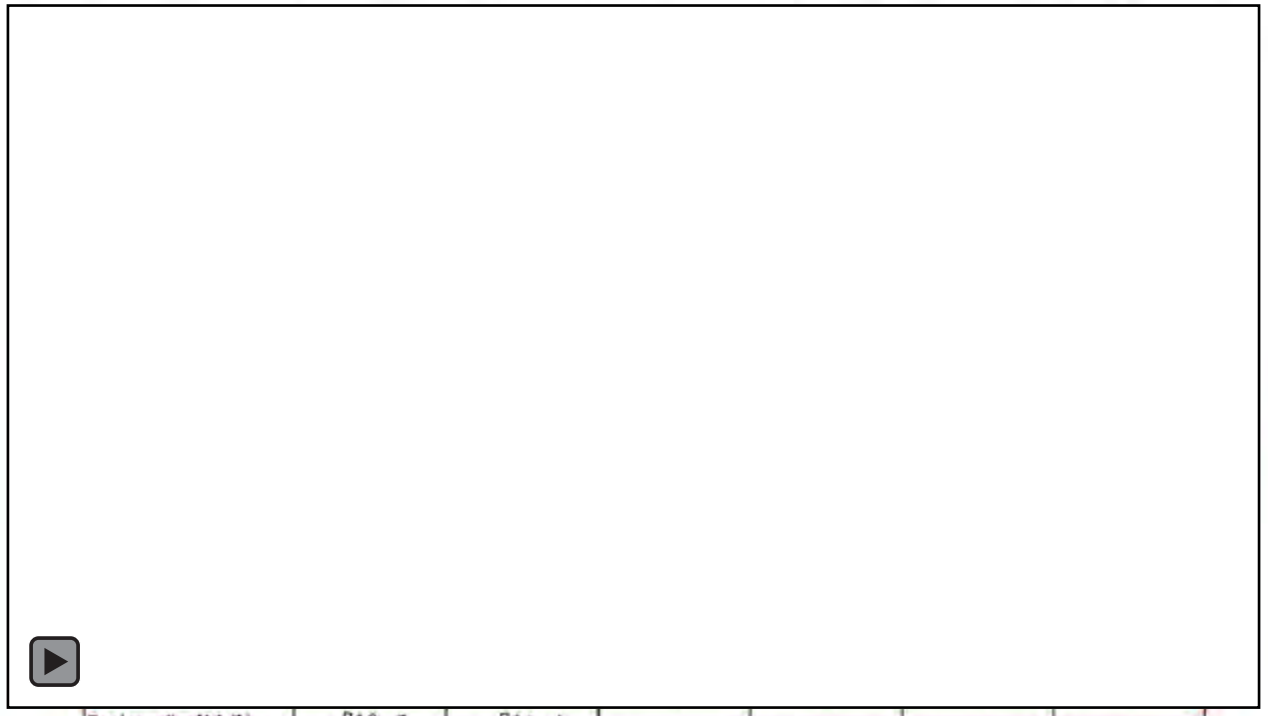
Target : Mercury

Sampling No. or Name		ST. 1		ST. 1 Duplicate									
Pump No.		303		304									
Column No.		6		7									
Sodalime No.		1		2									
Column position Info. (If necessary)		—		—									
No.	Date & Time	Instantaneous flow rate	Total Vol. (L)	Instantaneous flow rate	Total Vol. (L)	Instantaneous flow rate	Total Vol. (L)	Instantaneous flow rate	Total Vol. (L)	Instantaneous flow rate	Total Vol. (L)	Instantaneous flow rate	Total Vol. (L)
0	(pre-initiation default)	0.5	—	0.5	—								
1 (start)	10/11 11:20	0.5	0	0.5	0								
2	13:20	0.5	60.1	0.5	60.1								
3	16:20	0.5	150.1	0.5	150.2								
4	10/12 9:20	0.5	660.2	0.5	660.3								
5													
6													
7													
8													
9													
10 (end)	11:20	—	720.0	—	720.1								
Total sampling Vol. (L)		720.0		720.1									

Column No. of Travel Blank	Special instruction :
8. 9. 10	

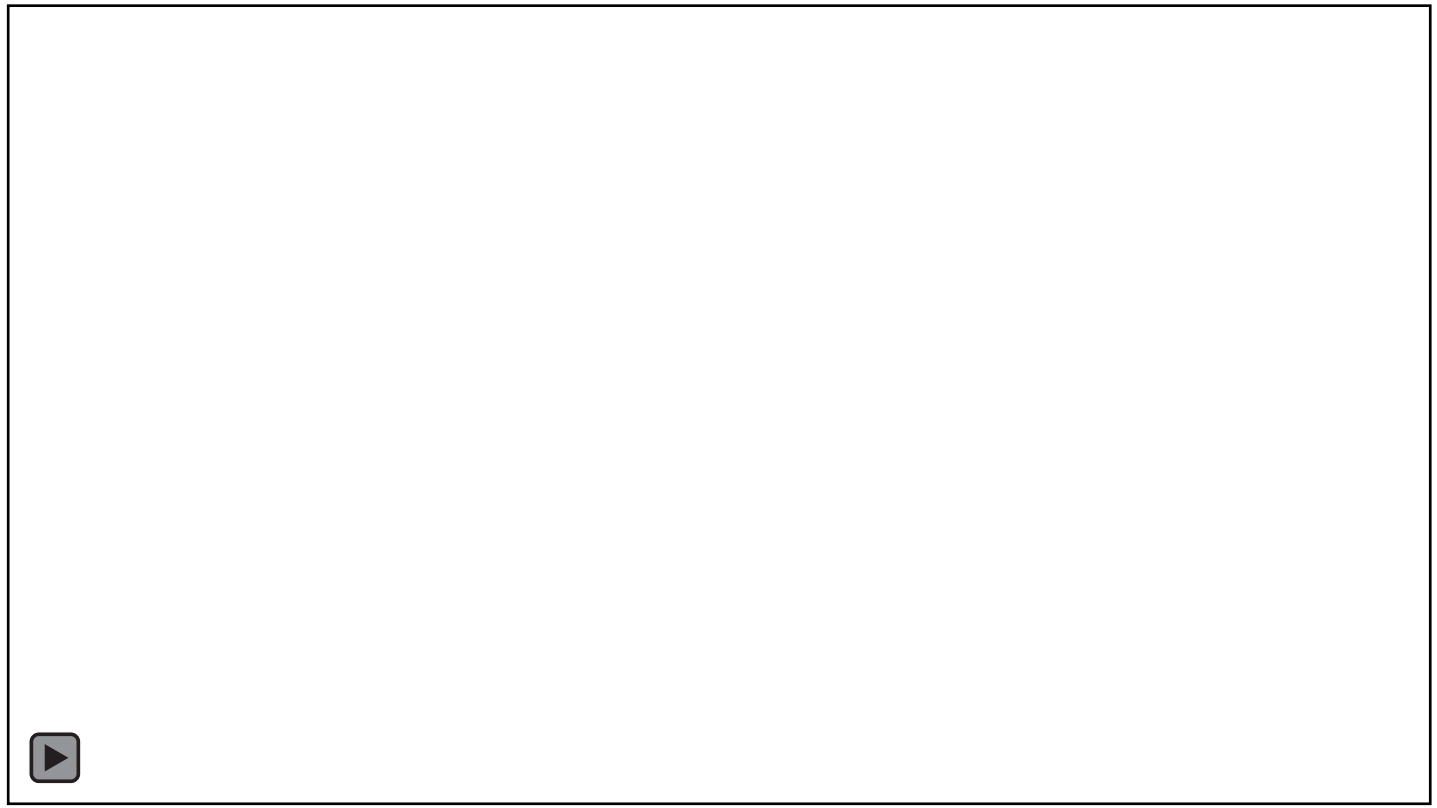
Site Inspection during Sampling

- For early detection of any error of the survey, revisit and inspect the survey site during the sampling



Total sampling Vol. (L)	720.0	720.1				
Column No. of Travel Blank 8. 9. 10	Special instruction :					

End of Sampling, Cartridge Collection



After sampling time (24 hours)

- ❑Turn off the pump
- ❑Record sampling volume
- ❑Open the field blank case
- ❑Take collected cartridge and put it in the case
- ❑Close the field blank case

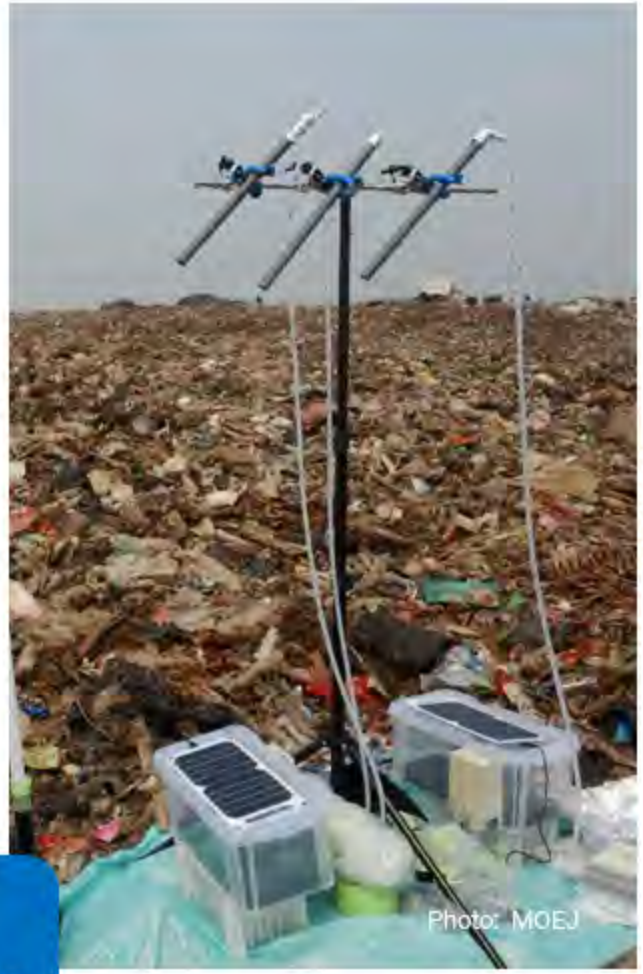
Duplicate Sampling

- To confirm the stability (precision) of the survey, 1 pair of duplicate sampling on 10 samplings is recommended.
- Deploy 2 (or more) cartridges side by side.

Atmospheric Surveys in Special Situation

Needs of Atmospheric Mercury Survey / Monitoring

- Atmospheric mercury survey / monitoring is also required other than general environment.
- For example:
  - In / near the mercury using or emitting facility.
  - Work environment using mercury.
  - Waste dumping site.
  - Accidental situation (e.g., mercury is spilled out).



In such situation, there may be especially high concentration of mercury.

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Application of Manual Active Sampling Method

Owing to its mobility, manual active sampling is applicable (and useful) for the survey / monitoring of special situation / sites.

- ❑ Easy to carry sampling equipment
- ❑ Quick to set-up
- ❑ Require small space

However, following should be noted:

- High mercury concentration
- Interfering substances

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High Concentration of Mercury (1/2)

- In some cases, such as work environment using mercury or accidental spill-out field, atmospheric mercury concentration may be **especially higher than general environment** (it is sometimes thousands of times higher).
- Mercury amount of these samples sometimes **exceeds the range of calibration curve**, or measurement range of the instrument.

High Concentration of Mercury (2/2)

- Check the upper limit of measurement of the instrument
- If a very high concentration is expected:
  - Reduce the sample flow rate (minimum: 0.1 L/min).
  - Make sampling time shorter.
  - (On measurement) analyse higher concentration of standard.
- If the level of mercury concentration is unpredictable, it is effective to collect multiple samples with different sampling volumes.

Keep in mind collected atmospheric mercury sample cannot be “diluted” on measurement.

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Interfering Substances for Mercury Measurement

- Restricting the capture of mercury, and causing damage the gold cartridge
  - Aerosol
- Interfering the CVAAS measurement
  - Halogenate gas
  - Nitrogen Oxide (NOx)
  - Sulphur Oxide (SOx)
  - Organic compound gas
  - (High moisture)
  - (Ozone)

High amount of aerosol causes damage to gold cartridge and decreases its recovery rate of mercury.

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Countermeasure for Interfering Substances

- Particle filter

- Gas scrubber (in front of the soda lime trap)

- Larger soda-lime trap

If electricity is available, heating the gold cartridge (around 100-150 °C) is effective.

Measurement, Data Processing and QA/QC

Measurement of Gold Amalgamation Cartridge

Diagram of Measuring Instrument

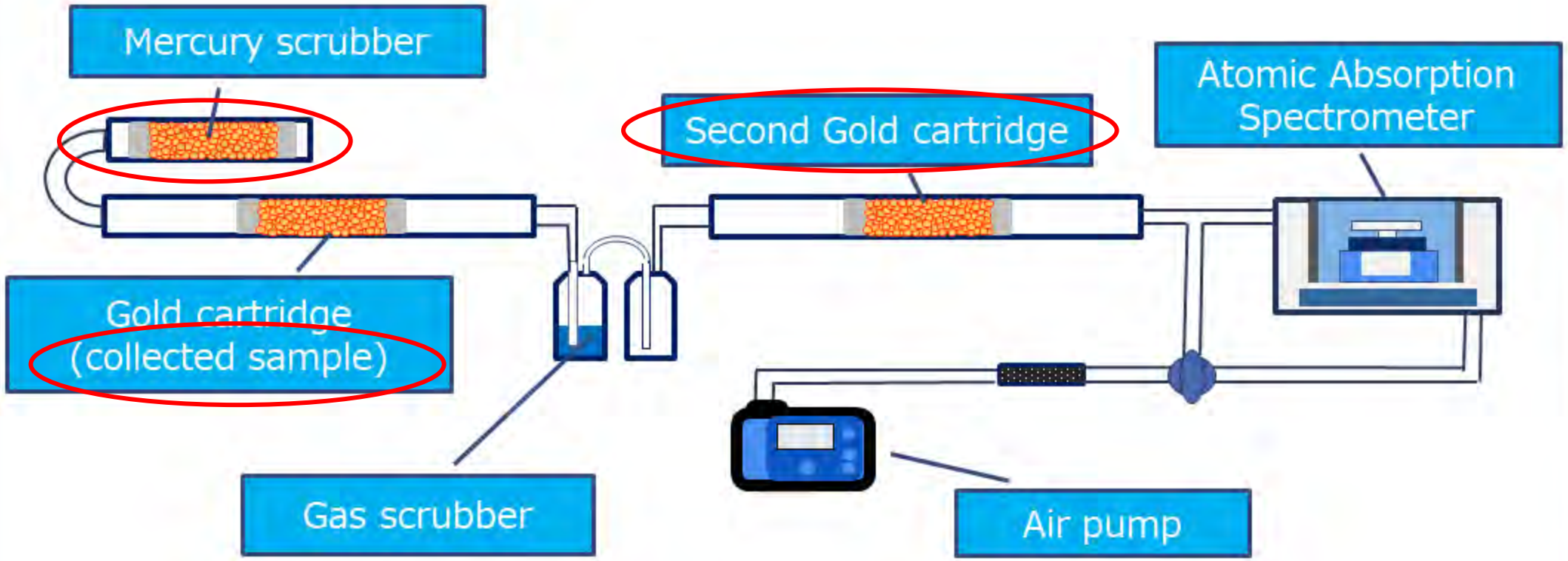

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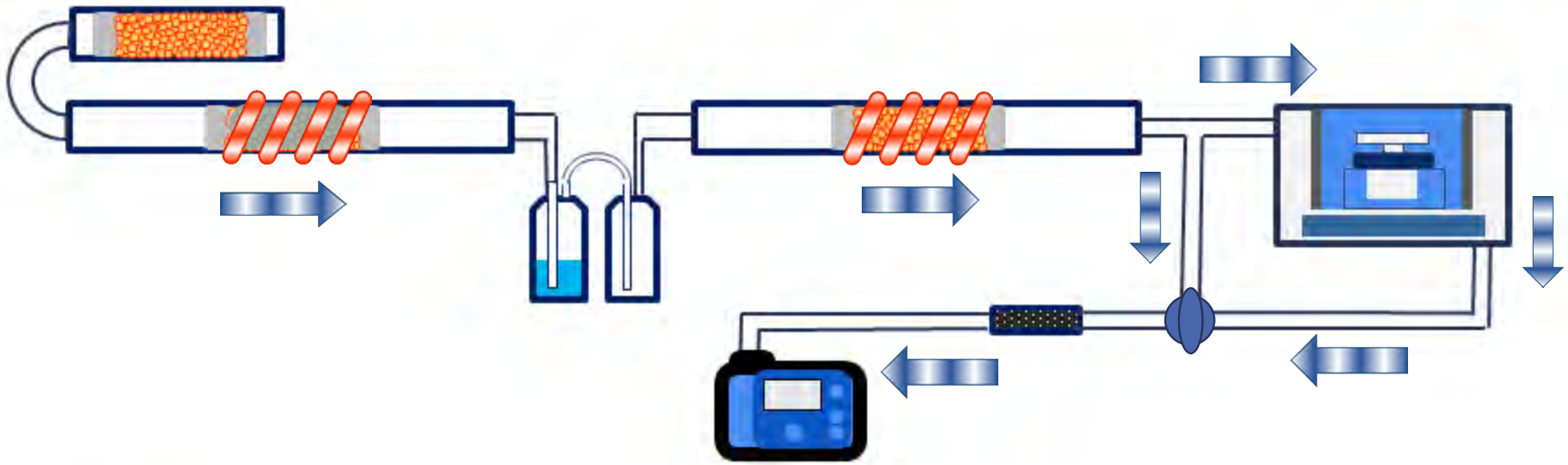
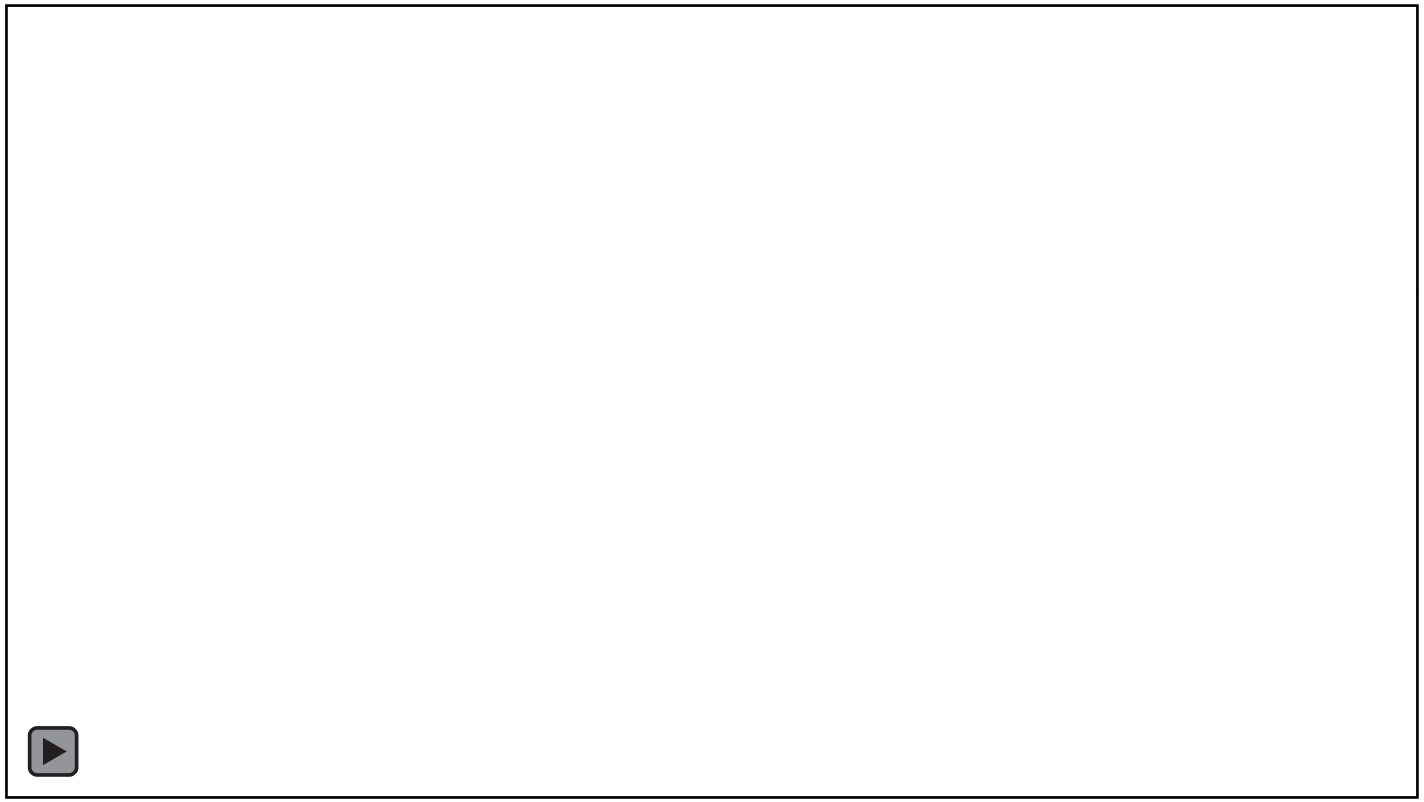
Diagram of Measuring Instrument



No reagents, consumable items and carrier gas (just only air)

CVAAS Measurement

Thermal Desorption CVAAS Measurement



- ❑Operation blank
- ❑Standard
- ❑(Field blank)
- ❑Sample
- ❑(Moderate concentration standard / 10 sample)

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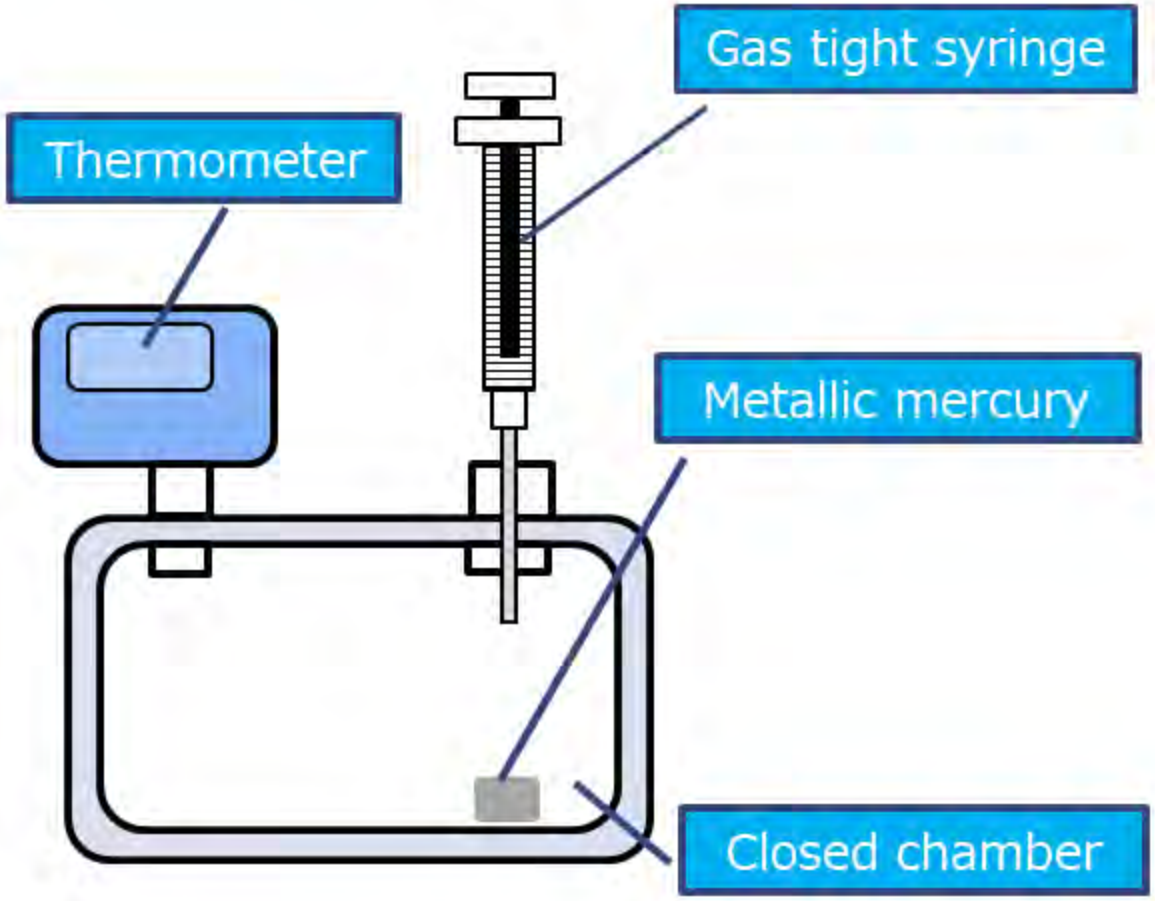
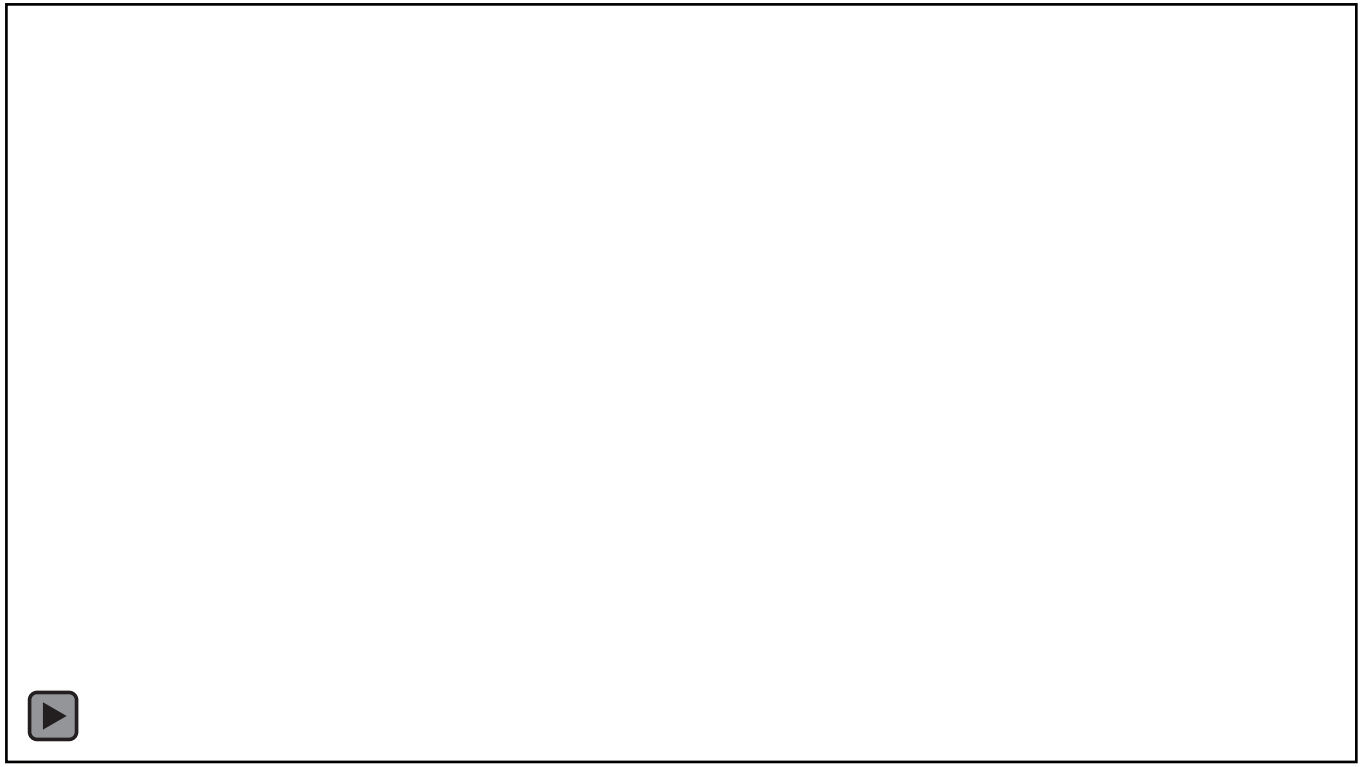
Gaseous Mercury Standard



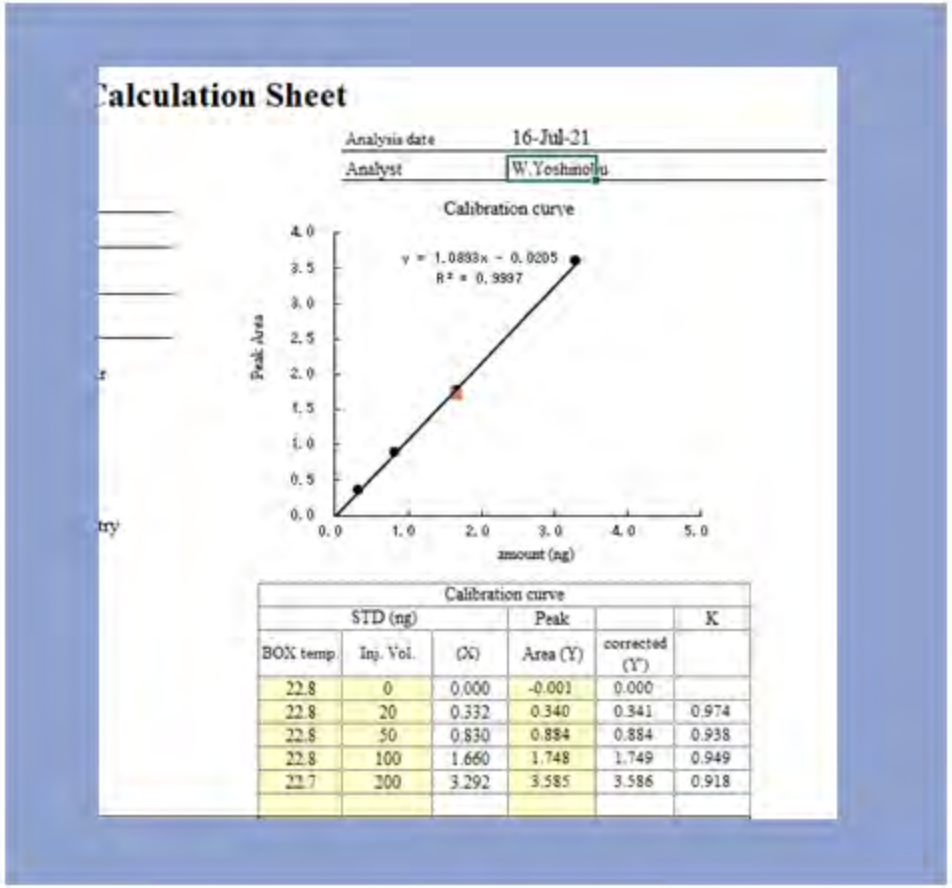
- Draw saturated gaseous mercury from closed chamber containing metallic mercury
- Mercury amount in the drawn gas is known from the volume and temperature of the gas

Making Standard for Calibration Curve (1/2)



- ❑ Record the temperature and saturated vapour pressure of the chamber
- ❑ Draw the saturated mercury gas
- ❑ Inject the mercury gas into the CVAAS

Making Standard for Calibration Curve (2/2)



Calculation Sheet

Analysis date 16-Jul-21

Analyst W.Yoshinoiu

Calibration curve

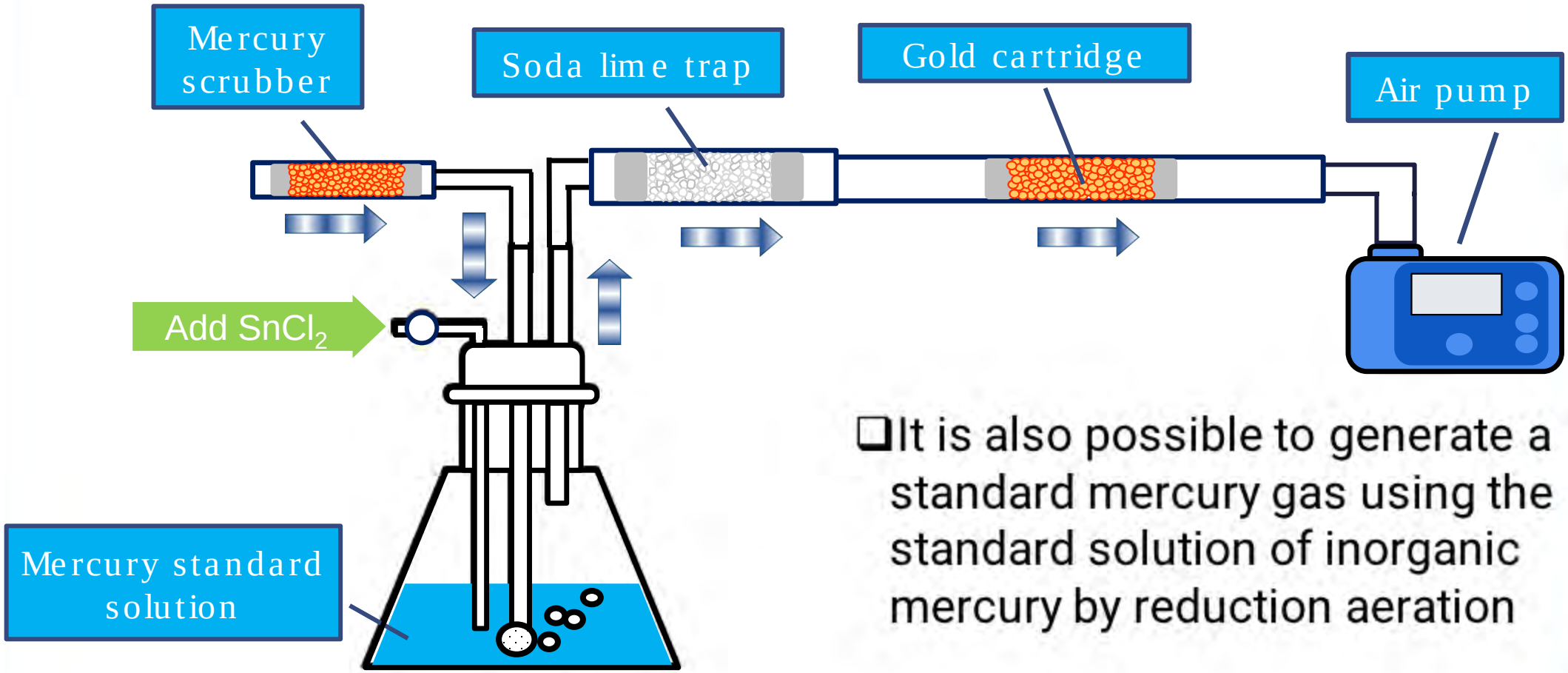
Calibration curve					
STD (ng)			Peak		K
BOX temp.	Inj. Vol.	(X)	Area (Y)	corrected (Y')	
22.8	0	0.000	-0.001	0.000	
22.8	20	0.332	0.340	0.341	0.974
22.8	50	0.830	0.884	0.884	0.938
22.8	100	1.660	1.748	1.749	0.949
22.7	200	3.292	3.585	3.586	0.918

- Make the standards for calibration curve by converting the saturated gaseous mercury added

Collected atmospheric sample can be analysed **only once**

Make standards that can certainly cover the amount of mercury in the sample

Standard Preparation by Reduction Aeration



- It is also possible to generate a standard mercury gas using the standard solution of inorganic mercury by reduction aeration

Data Processing and QA/QC

Data Processing (Calculation)

$$C = \frac{A_{sam} - Abl}{V_{sam} \times Tst/Tsam \times Psam/101.3}$$

C: Sample concentration (ng/m^3)
A_{sam}: Calculated sample mercury mass (ng)
A_{bl}: Calculated blank mercury mass (ng)
V_{sam}: Sample volume (m^3)
T_{st}: Based temperature for conversion (K)
T_{sam}: Average temperature during sampling (K)
P_{sam}: Average air pressure during sampling (kPa)

- Blank: Operation blank or Field blank
- Temperature for conversion: Standard state (e.g., 0 °C 1 atm, 20 °C, 1 atm)

Operation Blank

- Should be confirmed in each measurement
- Usually, significantly large operation blank is not detected. (less than LOD)
- Prior to the sample measurement, it should be confirmed that the operation blank is low.

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Field Blank (Travel Blank) (1/2)

- Should be confirmed 1 time in 10 sampling operations (1 time is not 1 sample, usually 3 or more).
- Usually, field blank does not show significantly large value. However, it may be possible when the sample collection is conducted in the high concentration environment (e.g., nearby or in the mercury emission facility.

Field Blank (Travel Blank) (2/2)

- If the deviation among field blanks is small, it may be assumed that all collected samples are contaminated uniformly
- Average of field blank value can be subtracted from the measured amount of sample.

- **To calculate the standard deviation, 3 or more of field blank samplings simultaneously is recommended**

Either case of the followings is applicable:

- **10 x std. dev. of field blank is smaller than required LOQ**
- **Field blank subtracted sample concentration is larger than required LOQ**

Duplicate Sampling

- To confirm stability (precision) of the sampling, 1 duplicate survey in 10 samplings is recommended.
- Deploy 2 or more gold cartridges and conduct sampling at the same point and time

Each result should be within 30 % (15 % from average)
In many cases, the difference of duplicate is much smaller.

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Limit of Detection and Limit of Quantification

- LOD and LOQ should be confirmed prior to the survey.
- When the condition of the survey and analysis is changed (e.g., replace or major repair of the instrument), LOD and LOQ should be reconfirmed.
- Make 5 or more small amounts (usually, minimum of the point of calibration curve) of standard gas cartridge and measure them.

- **LOD = 3 x std. dev.**
- **LOQ = 10 x std. dev.**

In usual 24 hours sampling situation, LOD and LOQ are much smaller than the background level atmospheric concentration.

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Compiling Data

- Obtaining data is meaningless if it is not used.
- To use data efficiently, data should be compiled together with the ancillary information (e.g., date and time, site coordinate, whether data).
- Electronic files recorded with related data by location, year, etc.

Database which involves whole data is very effective, but more challenging.

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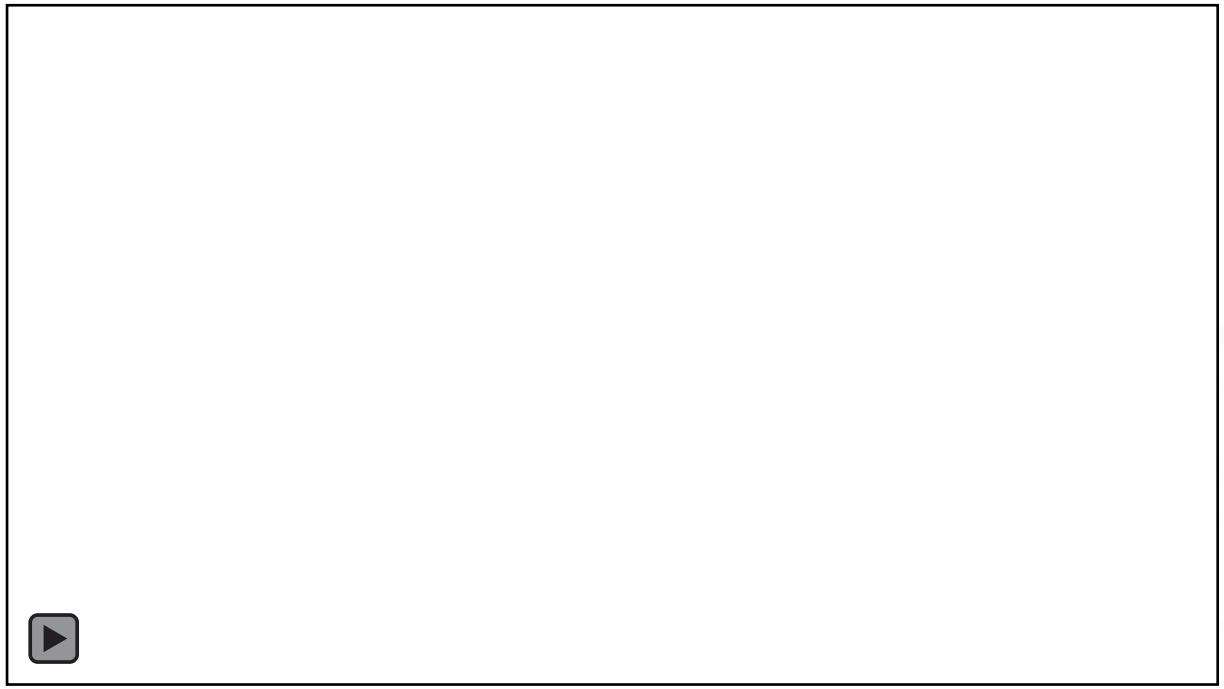
Maintenance and Calibration Methods

Confirmation of Recovery Rate of Gold Cartridge

When it is suspected the gold amalgamation trap cartridge is damaged, recovery of the cartridge should be checked.



- ❑Connect the cartridge and pump
- ❑Draw mercury standard gas around the middle amount of calibration curve from standard gas generator.
- ❑Turn on pump, aspirate air (0.5 L/min).
- ❑Add mercury gas into the cartridge.
- ❑Connect another gold cartridge (as a mercury scrubber)
- ❑Continue the pump dive (2 min.)

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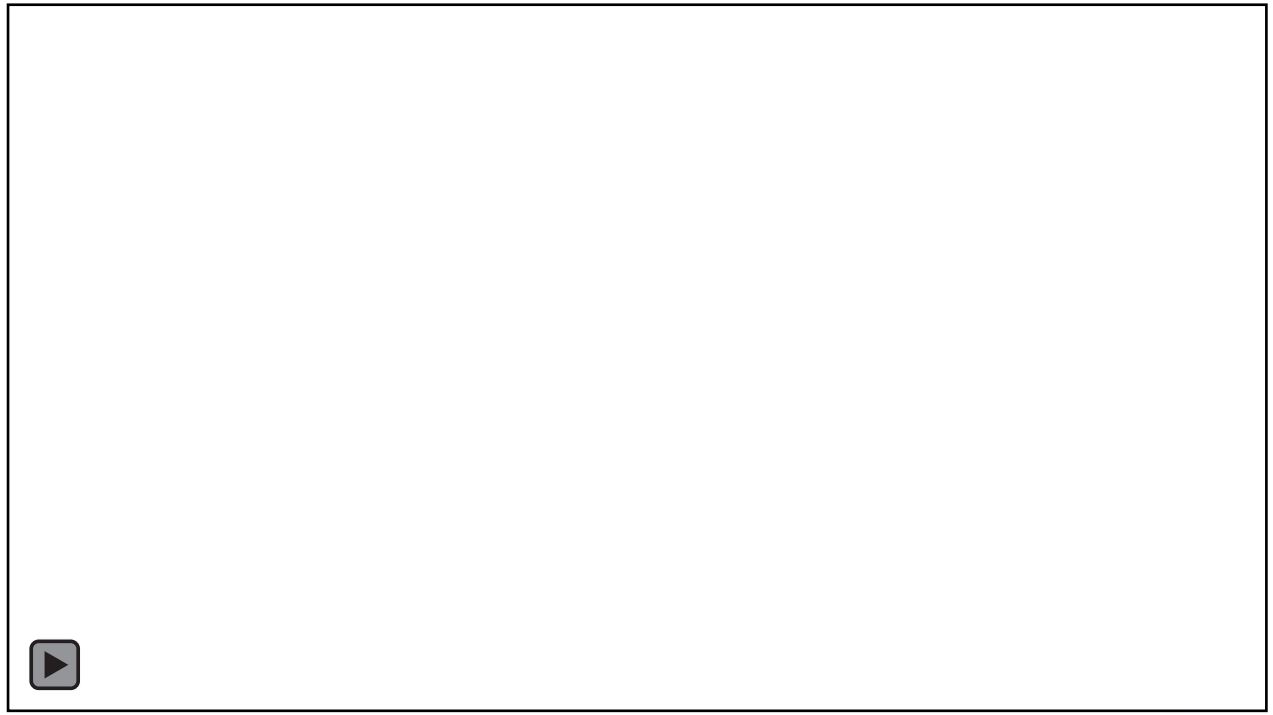
Confirmation of Recovery Rate



- ❑2 min. Later, remove the cartridge from the pump.
- ❑Measure the cartridge and standard for calibration curve.
- ❑Compare the analyzed concentration and added mercury amount and calculate the recovery.

If the recovery rate is low, cartridge should be cleaned.

Cleaning of Damaged Gold Cartridge (1/2)

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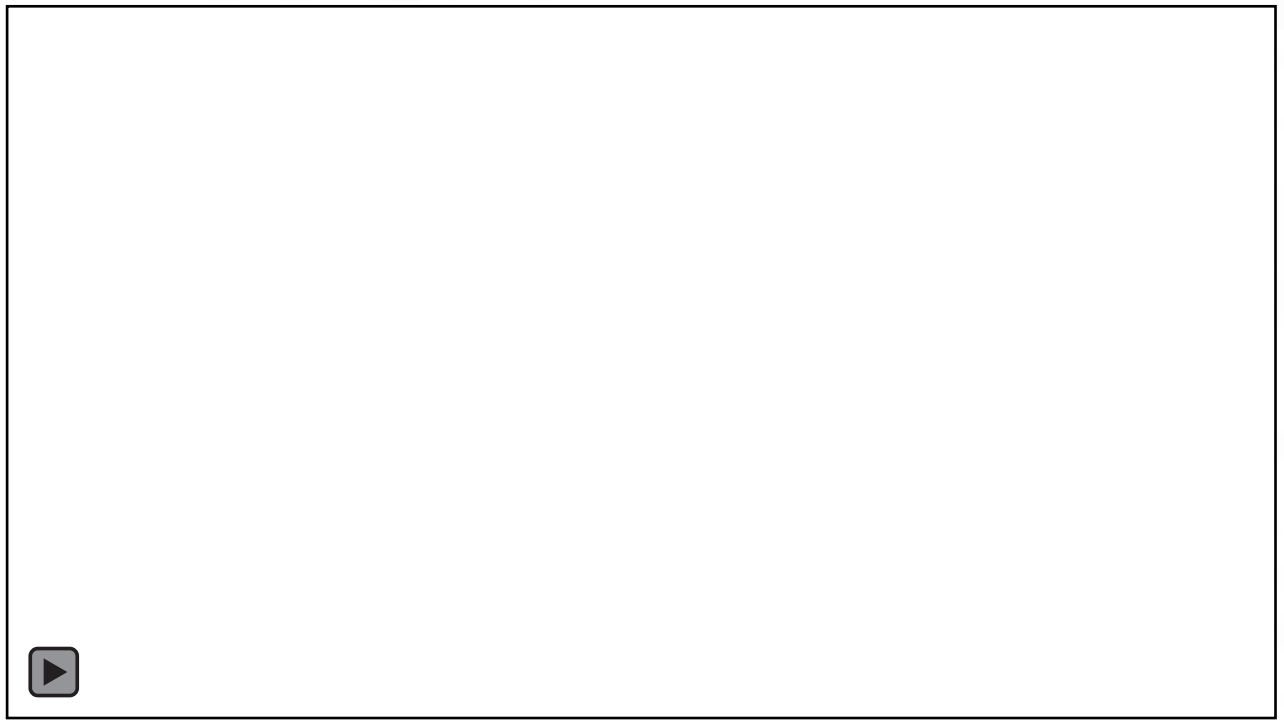
Cleaning by alcohol:



- ❑Prepare methanol or ethanol and cotton swab.
- ❑Wipe the outside of the tube.
- ❑Wipe inside of the tube by alcohol dipped cotton swab.
- ❑Wipe the new dry cotton swab.
- ❑Keep the cartridge in room temperature until the alcohol is dry.

Cleaning of Damaged Gold Cartridge (2/2)

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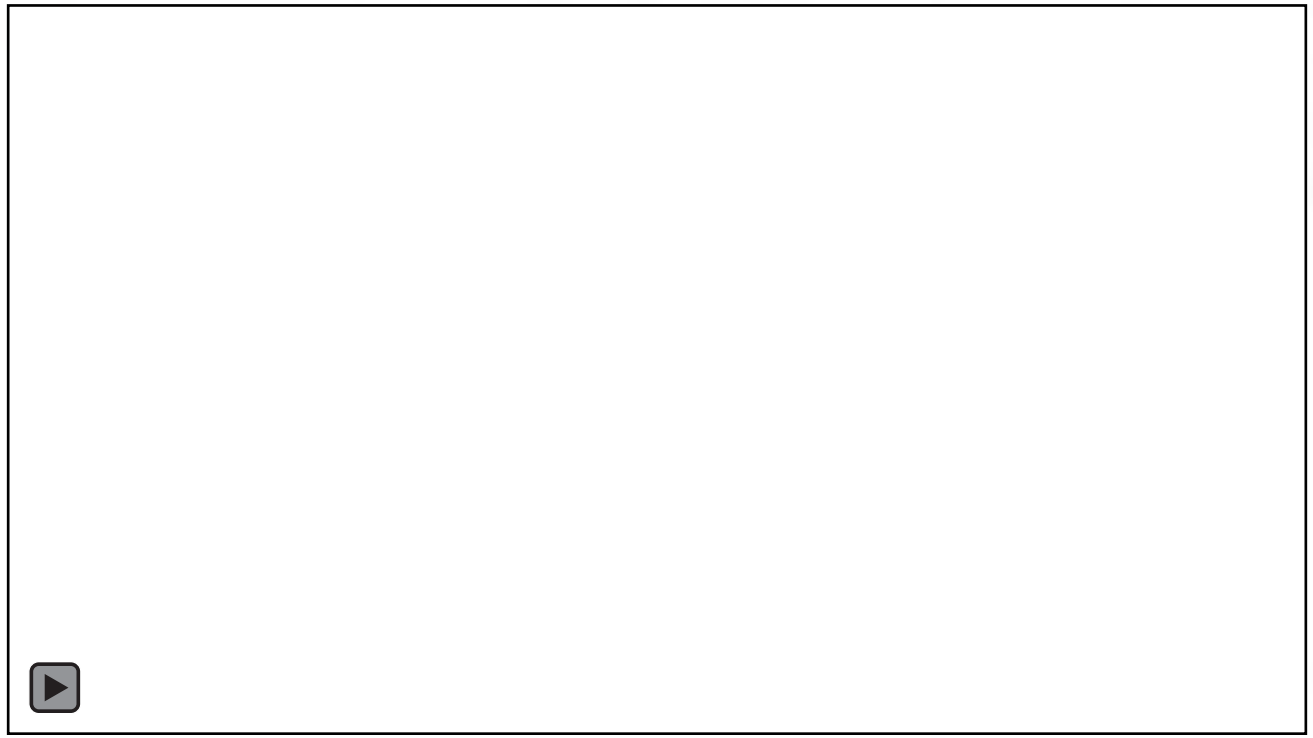
Heating cartridge in high temperature:



- ❑ Cartridge should be well washed.
- ❑ Place the cartridge on the durable dish (e.g., evaporating dish) Heat the cartridge in electric furnace (800 °C, 30 min.)
- ❑ After cooling to room temperature collect the cartridge from the furnace

After cleaning the cartridge, confirm the recovery rate.

Calibration of Flow Meter

soda lime

(with flow meter)

- ❑ Connect the standard flow meter to flow meter to be calibrated, pump and buffer tank.
- ❑ Turn on the pump and operate at the same flow rate as sampling (usually 0.5 L/min).
- ❑ Adjust the flow meter to match the rate of standard flow meter.

Calibration of Flow Meter

- ❑Drive the pump and record the indicated flow rate of flow meter multiple times.
- ❑Calculate the average and standard deviation (uncertainty) of the flow rate.